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**David W. Taylor Naval Ship Research and Development Center**

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Ship Materials Engineering Department

IR Report



# ESCA STUDIES OF MARINE CONDITIONING FILMS

by

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Immersion of a solid surface into a body of natural water exposes the surface to both the water itself and to a variety of dissolved materials. Because the adsorption process is usually faster than perceived corrosion or biological colonization, the degree to which the adsorbed layer affects subsequent events is important in control of biofouling and corrosion of naval equipment. In this report, Electron Spectroscopy for Chemical Analysis (ESCA) studies of the nature of the films formed during immersion in the natural water of the severn estuary are reported, and compared with ESCA signals obtained from samples of known substances which are expected to be similar to materials found in natural waters. The variables affecting the nature of the film on copper-nickel alloy included the biogeochemical state of the estuary, as determined by the season, and the electrochemical potential. Immersion of a sample of the plastic poly (vinyl

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chloride) (PVC) did not result in perceptible adsorption, but immersion of poly (fluoro-ethylene-propylene) (FEP Teflon™) resulted in a clear change of the carbon and oxygen ESCA signals, indicating significant adsorption. Both sulfides and protein-related components in natural saline waters have been implicated in accelerated corrosion of copper and its alloys. These findings indicate the detectability of these substances after short exposure, and show that their presence is related to the exposure conditions.

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## ABSTRACT

Immersion of a solid surface into a body of natural water exposes the surface to both the water itself and to a variety of dissolved materials. Because the adsorption process is usually faster than perceived corrosion or biological colonization, the degree to which the adsorbed layer affects subsequent events is important in control of biofouling and corrosion of naval equipment. In this report, Electron Spectroscopy for Chemical Analysis (ESCA) studies of the nature of the films formed during immersion in the natural water of the Severn estuary are reported, and compared with ESCA signals obtained from samples of known substances which are expected to be similar to materials found in natural waters. The variables affecting the nature of the film on copper-nickel alloy included the biogeochemical state of the estuary, as determined by the season, and the electrochemical potential. Immersion of a sample of the plastic poly [vinyl chloride] (PVC) did not result in perceptible adsorption, but immersion of poly [fluoro-ethylene-propylene] (FEP Teflon™) resulted in a clear change of the carbon and oxygen ESCA signals, indicating significant adsorption. Both sulfides and protein-related components in natural saline waters have been implicated in accelerated corrosion of copper and its alloys. These findings indicate the detectability of these substances after short exposure, and show that their presence is related to the exposure conditions.



## ADMINISTRATIVE INFORMATION

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## ACKNOWLEDGEMENT

We acknowledge and appreciate the efforts of L. Aprigliano and R. Stockhausen in operation of the ESCA equipment and for helpful discussions.

## INTRODUCTION

Immersion of a solid surface into a body of natural water exposes the surface to a variety of dissolved materials as well as to the water solvating them. If the dissolved materials are surface active, they will tend to adsorb upon the immersed surface and, in doing so, change the surface properties of the immersed interface. Because the adsorption process is usually faster than perceived corrosion or biological colonization, the degree to which the adsorbed layer affects subsequent events is important in control of biofouling and corrosion of naval equipment. An earlier report [1] indicated that the ESCA (Electron Spectroscopy for Chemical Analysis) and AES (Auger Electron Spectroscopy) techniques could detect formation of organic surface films on copper, nickel, and titanium as a result of immersion in commercial bacteriological medium, and the ratios of the atoms in the surface region were determined. The results indicated that adsorbed films covered the nickel and titanium surfaces, but a thicker film of a cupro-organic complex formed on copper. In this report, ESCA studies of the nature of the films formed during immersion in the natural water of the Severn estuary are reported, and compared with ESCA signals obtained from samples of known substances which are expected to be similar to materials found in natural waters. The immersions were performed under cathodically protected and freely corroding conditions, and at different seasons.

## MATERIALS AND METHODS

Samples of copper-nickel alloy (90% Cu, 10% Ni) and the plastics PVC [poly(vinyl chloride)] and FEP [poly(fluoro ethylene-propylene)], all 2.2 $cm^2$, were immersed in 1500 ml of filtered water from the local estuary, ie, the Severn River at the David Taylor Research Center, Annapolis, Md. Estuarine water was passed through

a 0.2 micrometer filter before exposures to prevent colonization of the surfaces by estuarine microorganisms. After the desired time of exposure, the surface of the water in which the sample was immersed was swept clean to remove any surface active microlayers at the air-water interface. The adsorbent sample was then withdrawn and drained by standing on edge on a pad of clean filter paper, and then air-dried. Samples of the alloy were held at the freely corroding potential or at a potential corresponding to cathodic protection (-0.28 volts versus the standard calomel electrode) during immersion, using a Princeton Applied Research potentiometric analyzer. Immersions of the alloy were during March and during May 1986. The PVC and FEP samples were also immersed in May 1986.

For comparison, water solutions were made of known materials obtained from commercial sources and then allowed to dry on glass plates so as to form thick films. The known materials were the protein bovine serum albumin (BSA), the common sugar sucrose, the bacterial exudate xanthan gum, and an extract of a commercial preparation of humic acid with artificial sea water (salinity 12 parts per thousand). These materials were chosen because they represent dissolved organic matter inputs to estuarine and coastal waters.

## ELECTRON SPECTROSCOPY

ESCA of all samples was performed with the Kratos XSAM 800 instrument at the Center. High resolution scans were made in the carbon, nitrogen, oxygen, and sulfur spectral regions, and graphs of photoelectron current versus binding energy were generated by the instrument's dedicated data processing station. The digital data were also available, and were processed further using a microcomputer and the Lotus 123 (™) program. Correlations of chemical shifts with molecular structure were made with the aid of published spectra [2]. Linear baselines were

constructed for each of the high resolution scans and intergrated areas under the peaks were calculated. Because ESCA peaks are not normally of the form of well-known functions such as Gaussian or Lorentzian functions [3], deconvolution of apparently bimodal signals was performed by subtracting a signal similar to the simplest signals from the observed signal. This resulted in a superimposed pair of apparently simple signals. The protein and May exposure of cupronickel yielded sulfur signals which were sufficiently complex that this approach is not sufficient, and more complex chemical environments of the sulfur atom are assumed.

## RESULTS AND DISCUSSION

The spectra of the known substances are shown in Figs. 1-13. Spectra of films adsorbed from the estuary are shown in Figs. 14-29. Ratios of areas under the peaks corresponding to the various types of atoms in the samples are shown in Table 1. The significance of the results may be appreciated through a comparison of the spectra of exposed materials with spectra of the known substances.

### KNOWN SUBSTANCES:

a. Sucrose - a sugar. This substance contains the elementary structure of carbohydrates. It consists of two saccharide units, each of which is a carbon chain with hydroxyl groups bonded to the carbon atoms. More complex carbohydrate structures are found in nature and consist of many saccharide units, some with additional chemical groups. However, they retain the elementary unit structure [4,5].

Fig. 1. shows the carbon signal of sucrose. It is quite symmetrical, and does not have pronounced changes of slope characteristic of superimposed signals. This is consistent with the known chemical structure in that all the carbon atoms are

bound to oxygen. The peak maximum is at 286 electron volts (ev) binding energy.

Fig. 2. shows the sucrose oxygen signal. There is a small secondary peak, whose area is estimated to be approximately one-tenth the area of the main peak. This may correspond to the "bridge" oxygen which links the two parts of the molecule. The main peak is at binding energy 532.5 ev. Consistent with its chemistry, there is no significant nitrogen or sulfur signal.

b. Bovine Serum Albumin (BSA) - a protein. This substance contains the polypeptide main chain and also the side-chain groups of the amino acids which are present in proteins. The organic components of natural waters are the result of interactions of biogenic inputs, and so can contain significant amounts of protein as well as reaction products of proteins with other dissolved organic matter.

Fig. 3. shows the carbon signal of BSA. The peak shape indicates a major component at 284 ev., characteristic of hydrophobic material, and a minor peak at ~ 287 ev., characteristic of more polar portions. The ratio of the component signal areas is estmated to be approximately 6.

Fig. 4. shows the oxygen signal of BSA. The peak shape indicates a major component at 530.5 ev, with a minor component at 527.5 ev. The ratio of the components is 2.5.

Fig. 5. shows the nitrogen signal of BSA. The peak shape is almost symetrical, although there is an indication of a small lower binding energy component with 1/10 of the signal area of the major component. The main component is at 399 ev, which is characteristic of reduced forms of nitrogen such as amines and amides, which are known to be present in proteins.

Schrader and Cardamone found a similar chemical shift for adsorbed bacterial medium on metal in earlier work [1]. Sulfur is present in proteins as sulfhydryl groups (-SH), which can react with metals and other reactive functional groups.

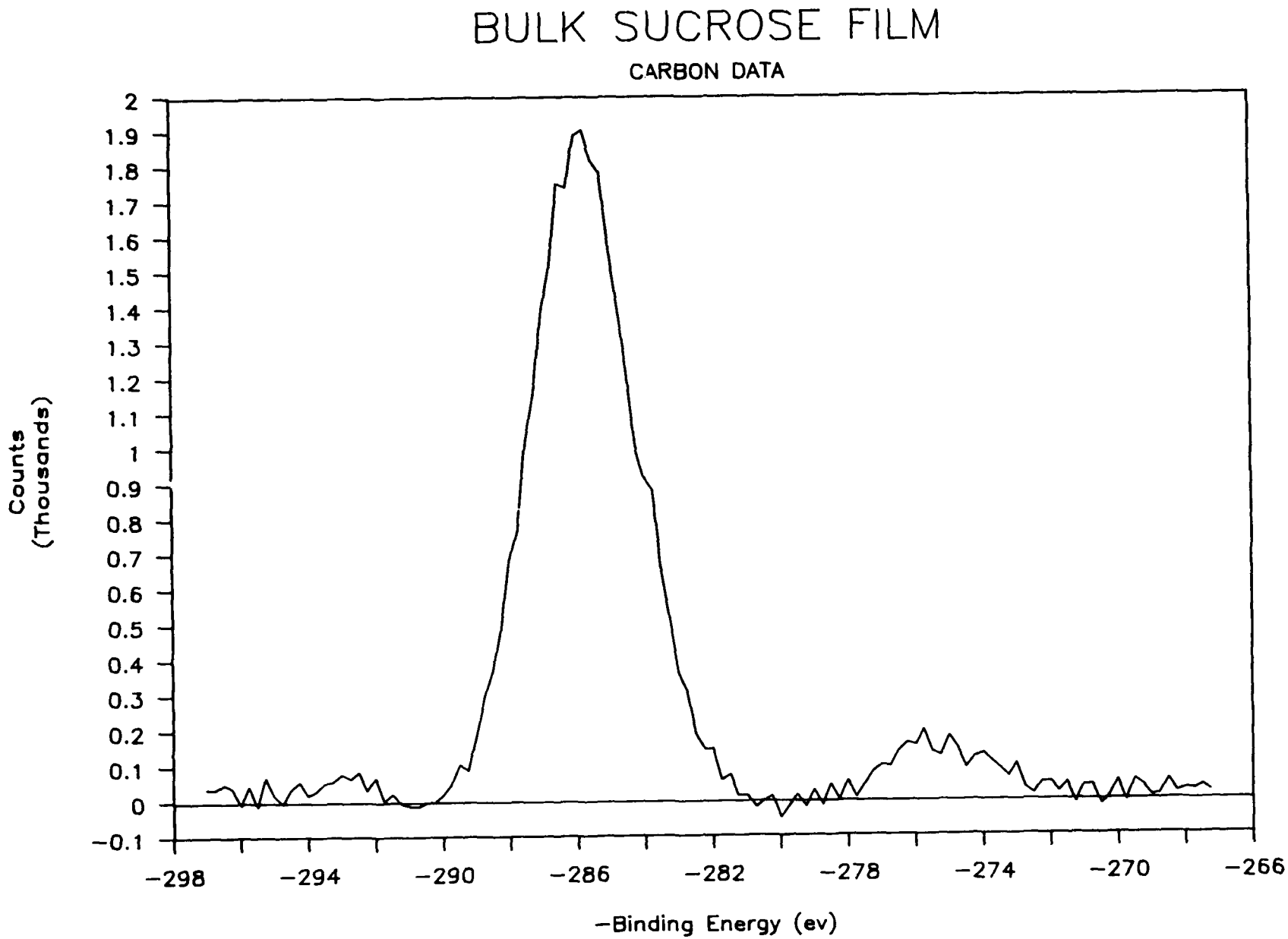


Fig. 1. ESCA Carbon Signal of Sucrose

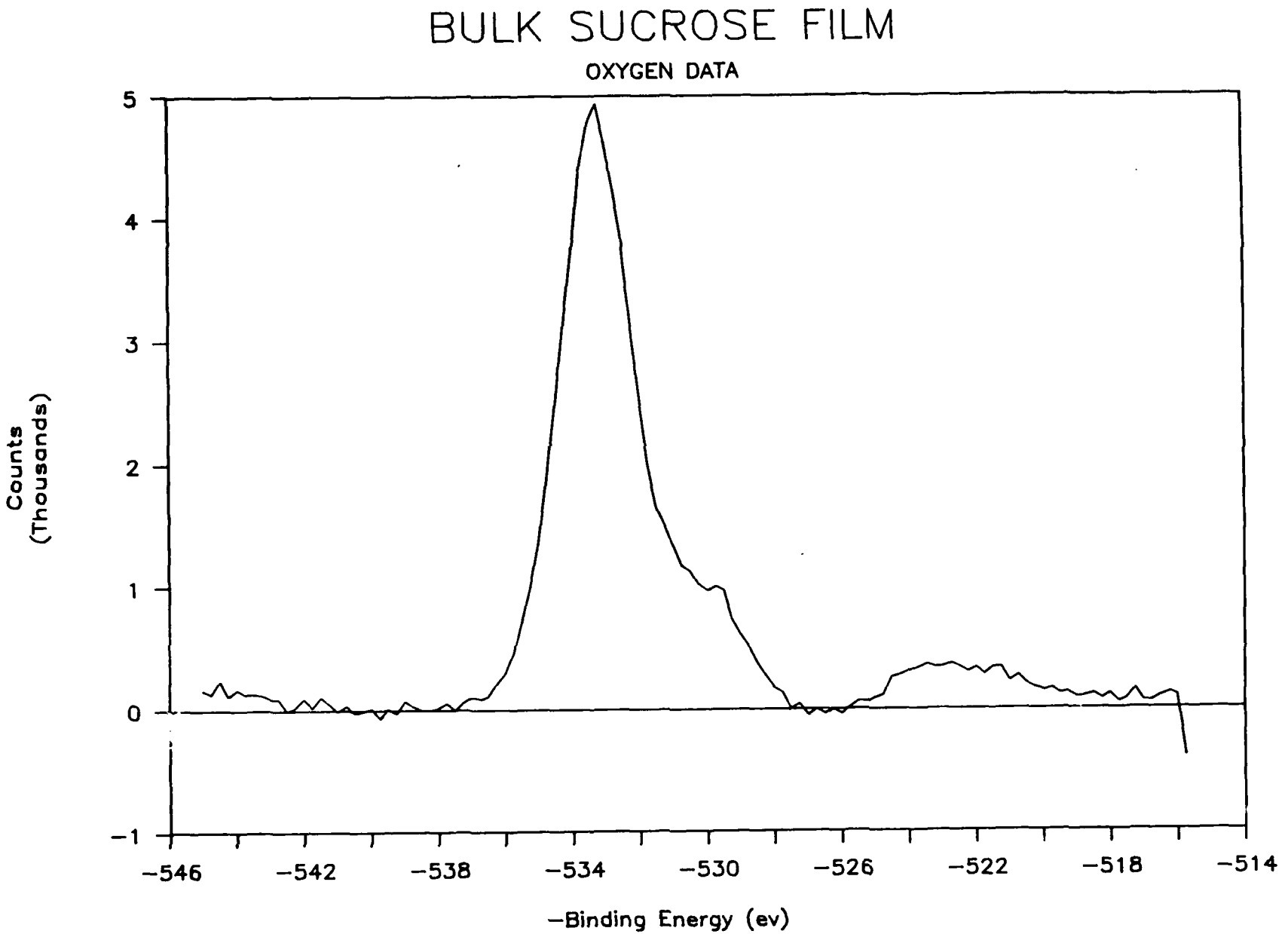


Fig. 2. ESCA Oxygen Signal of Sucrose

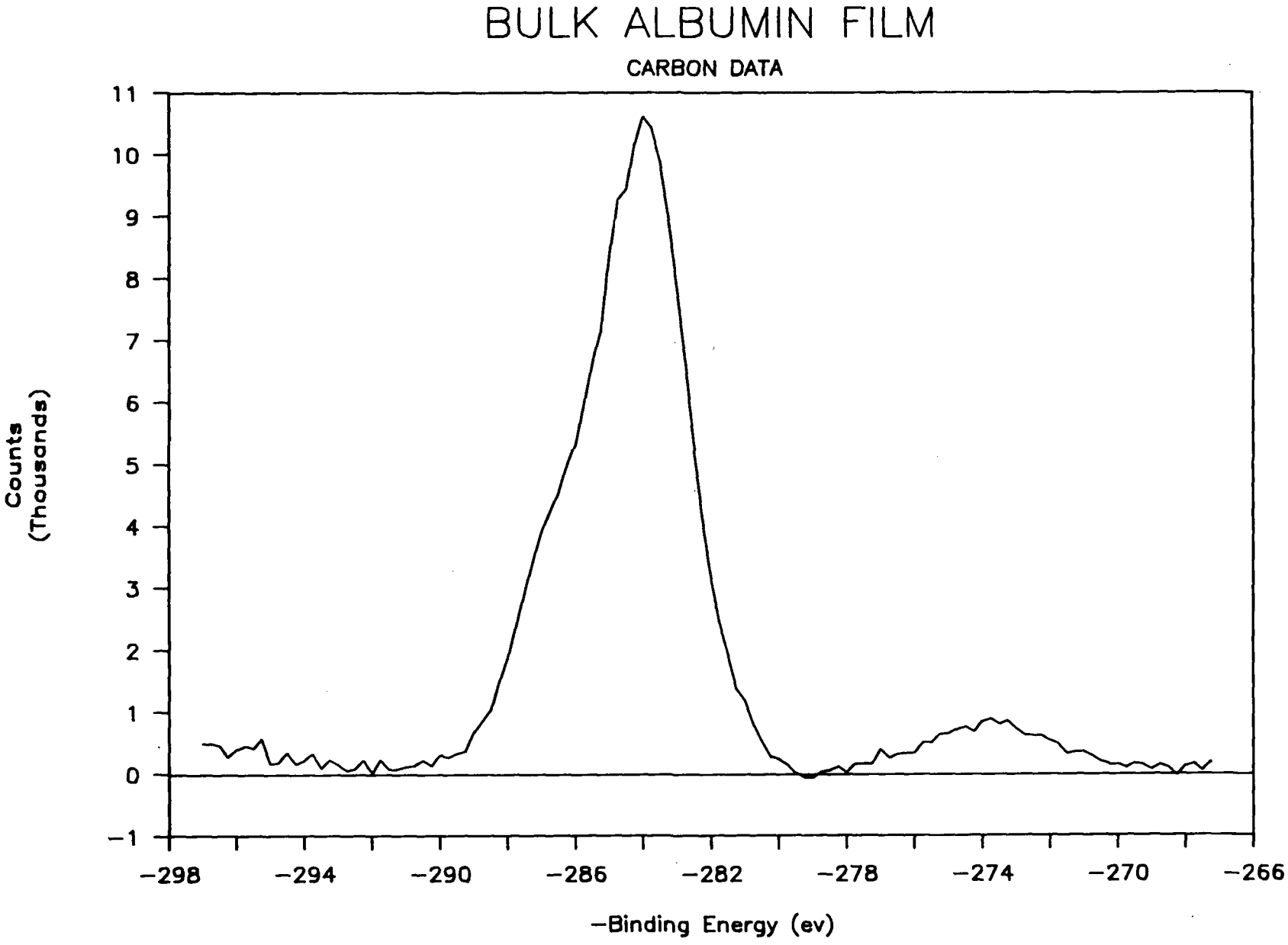


Fig. 3. ESCA Carbon Signal of BSA

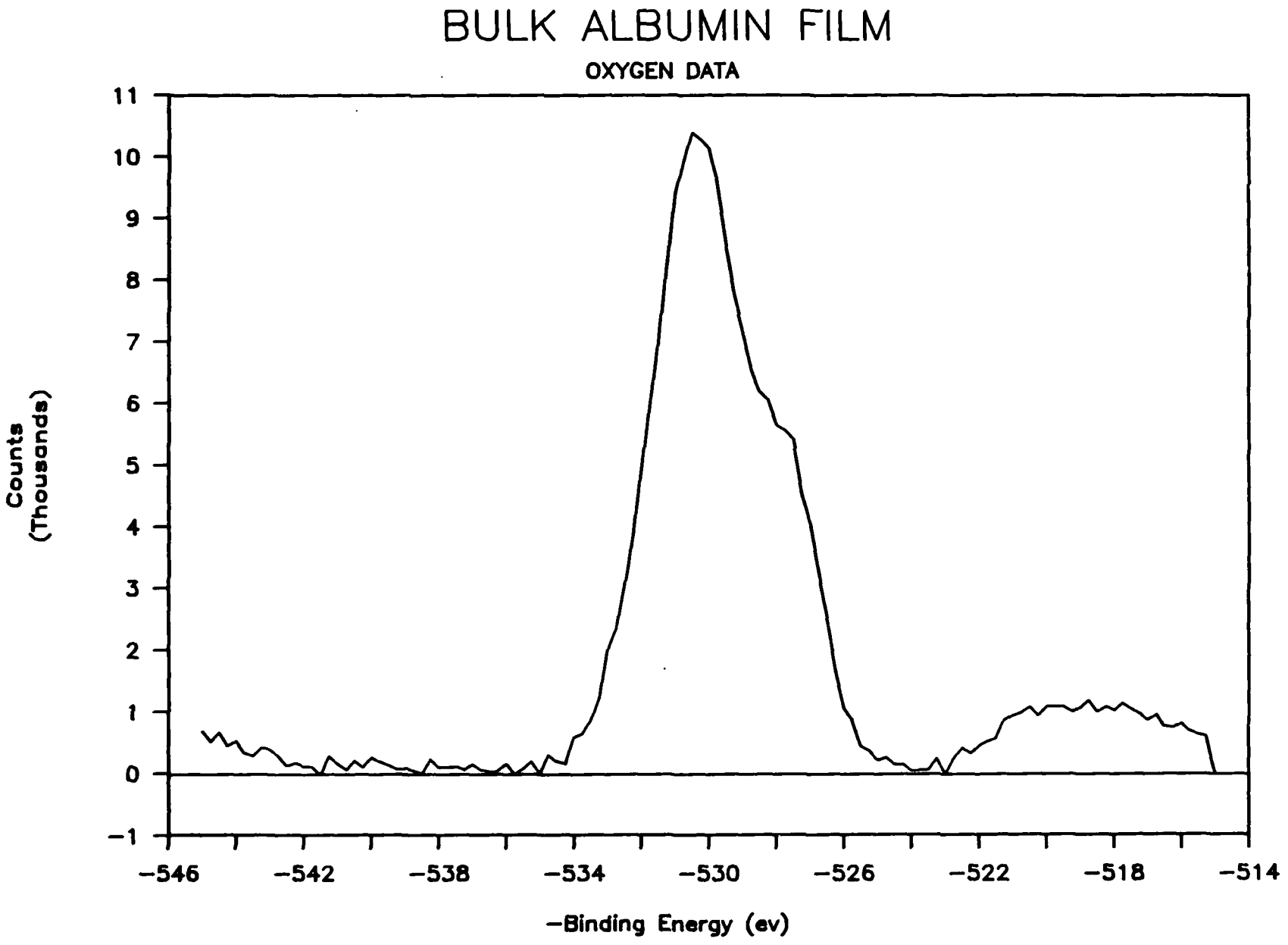


Fig. 4. ESCA Oxygen Signal of BSA

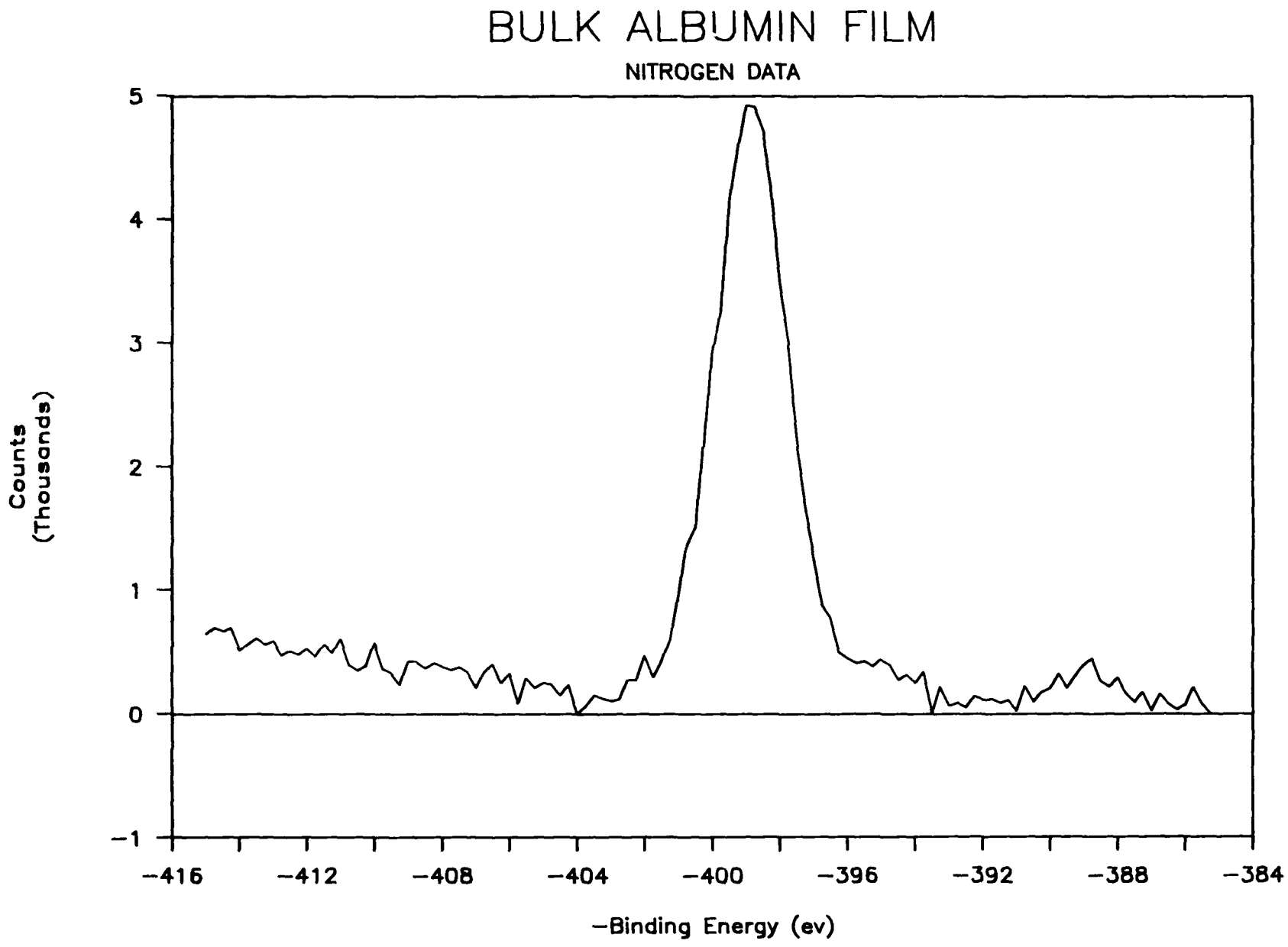


Fig. 5. ESCA Nitrogen Signal of BSA

It is also found as disulfide (-S-S-) groups, which form cross-links and loops that maintain strong structural bonds among the copolymeric peptide main chains which make up protein molecules. BSA is known to contain 17 -SS- and 0.7 -SH groups per molecule [6]. The -SH and -SS- signals are expected at 163-164 ev.

Fig. 6. shows the sulfur signal of BSA, which peaks at 164 ev. However, it is quite broad, and complex. The distribution of binding energies may be the manifestation of different chemical environments of these groups within the BSA molecule.

c. Gum Xanthan - [gum - x] - a bacterial exudate. It is produced by a species of marine bacterium. Secreted in large quantities by this particular organism, it is harvested commercially from cultures on an industrial scale. It is predominantly carbohydrate in nature, and of high molecular weight. As its name implies, it is viscous and "tacky" in concentrated solutions, which makes it interesting in the context of bacterial attachment and colonization of immersed surfaces.

Fig. 7. shows the carbon signal of gum - x. The main component is at 286 ev, similar to the sugar signal. However, a minor component ~ 1/10 signal area ratio) is evident at lower binding energy, and close to the value for the protein signal.

Fig. 8. shows the oxygen signal of gum - x. The maximum is at 532.5 ev, as in the sugar signal. It has 2.5 ev more binding energy than the protein signal. However, there is a minor component at 327.5 ev, to the extent of ~ 1/3 of the main peak. This chemical shift is similar to that found for the minor peaks of sugar and protein.

Fig. 9. shows the nitrogen signal of gum - x. It is a relatively weak signal, an order of magnitude weaker than the protein nitrogen signal. However, two peaks

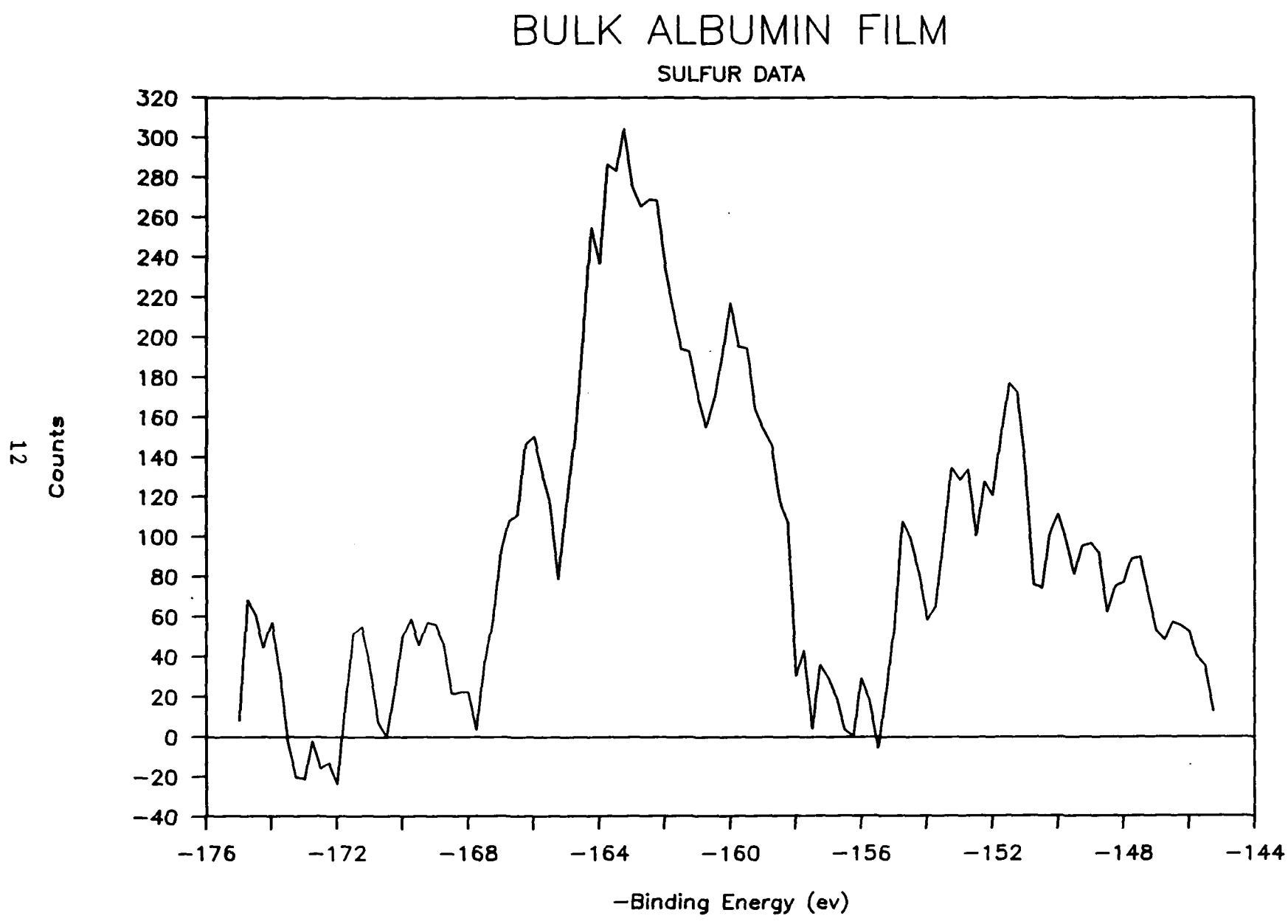


Fig. 6. ESCA Sulfur Signal of BSA

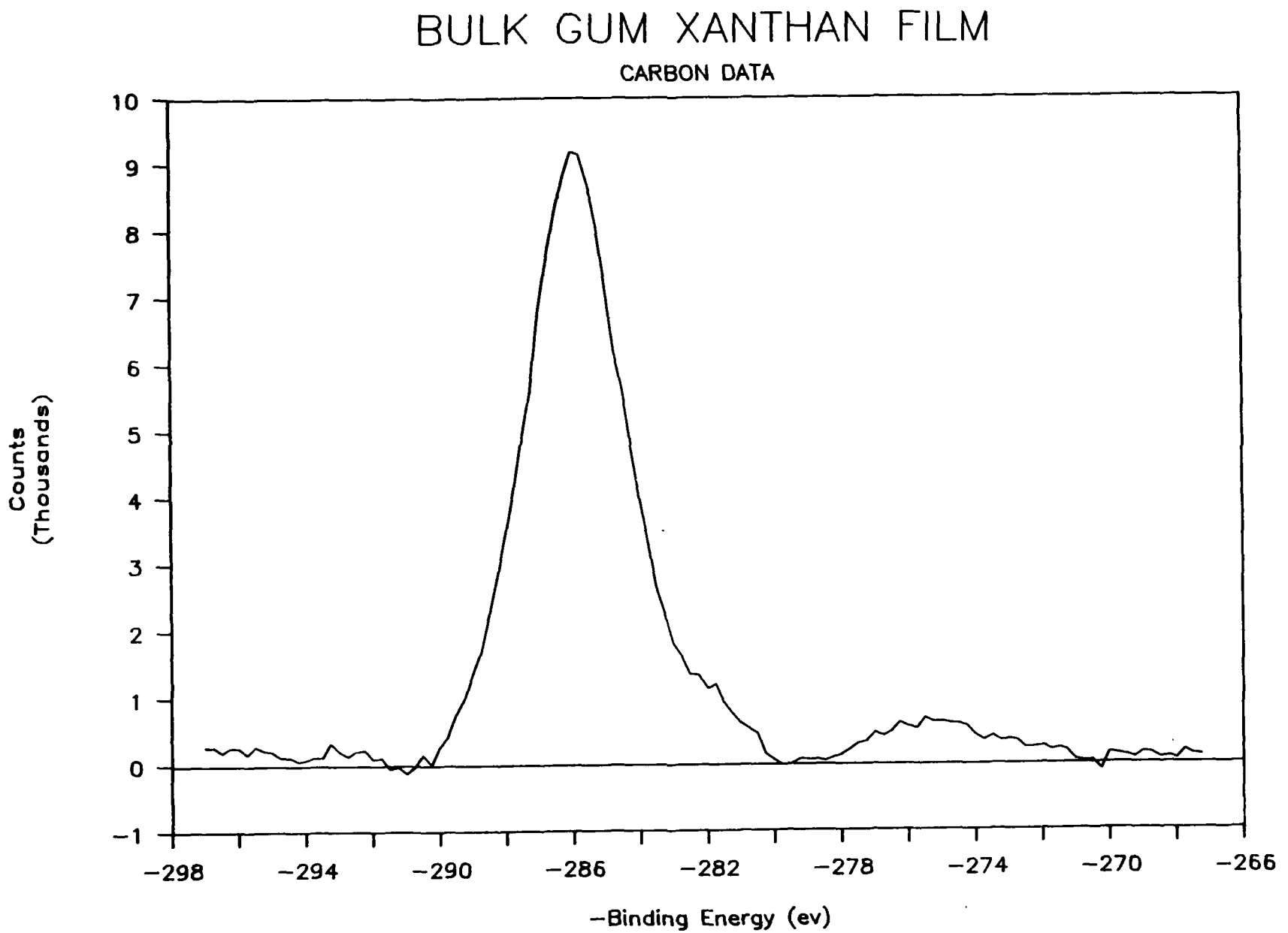


Fig. 7. ESCA Carbon Signal of Gum Xanthan

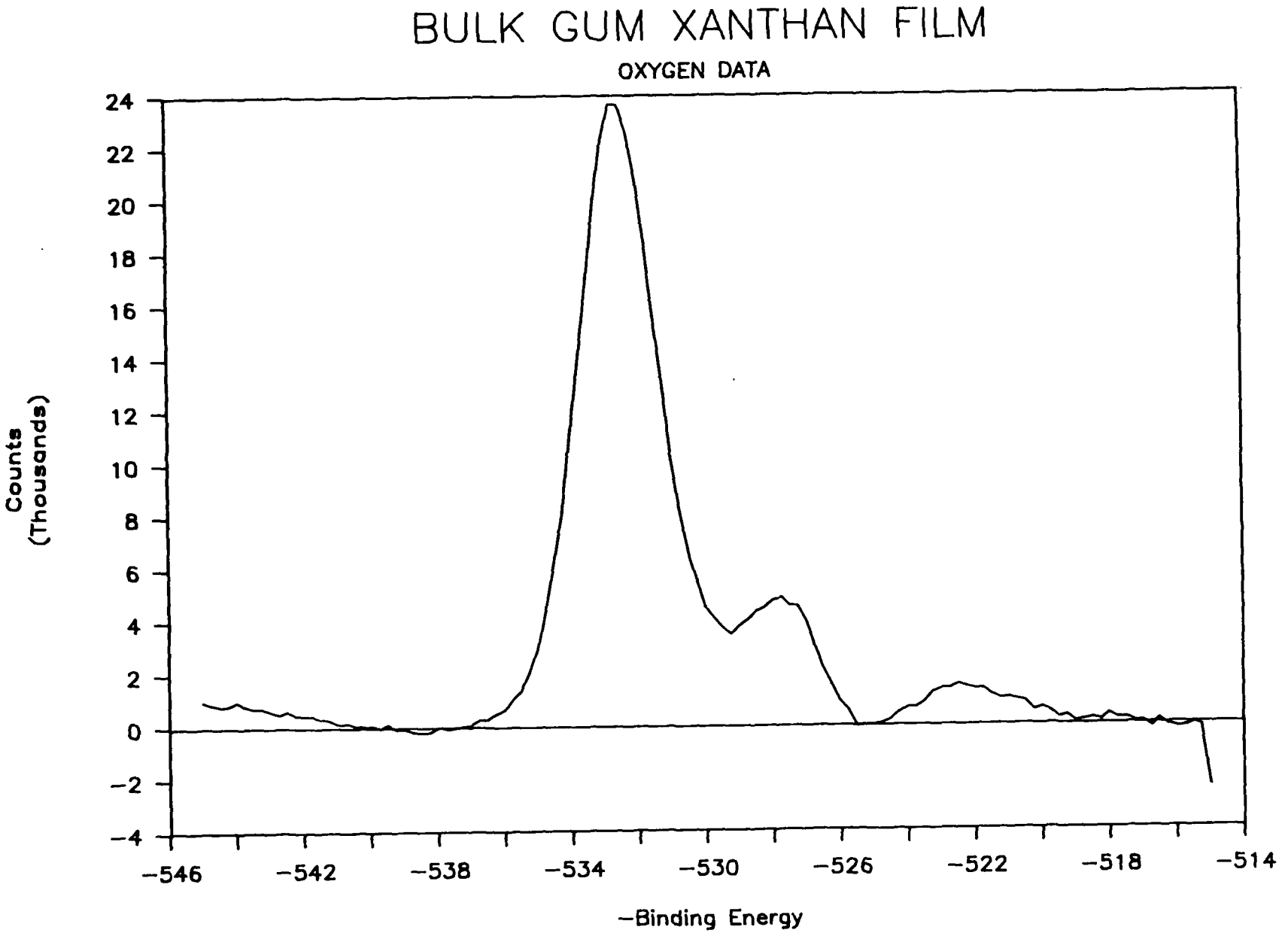


Fig. 8. ESCA Oxygen Signal of Gum Xanthan

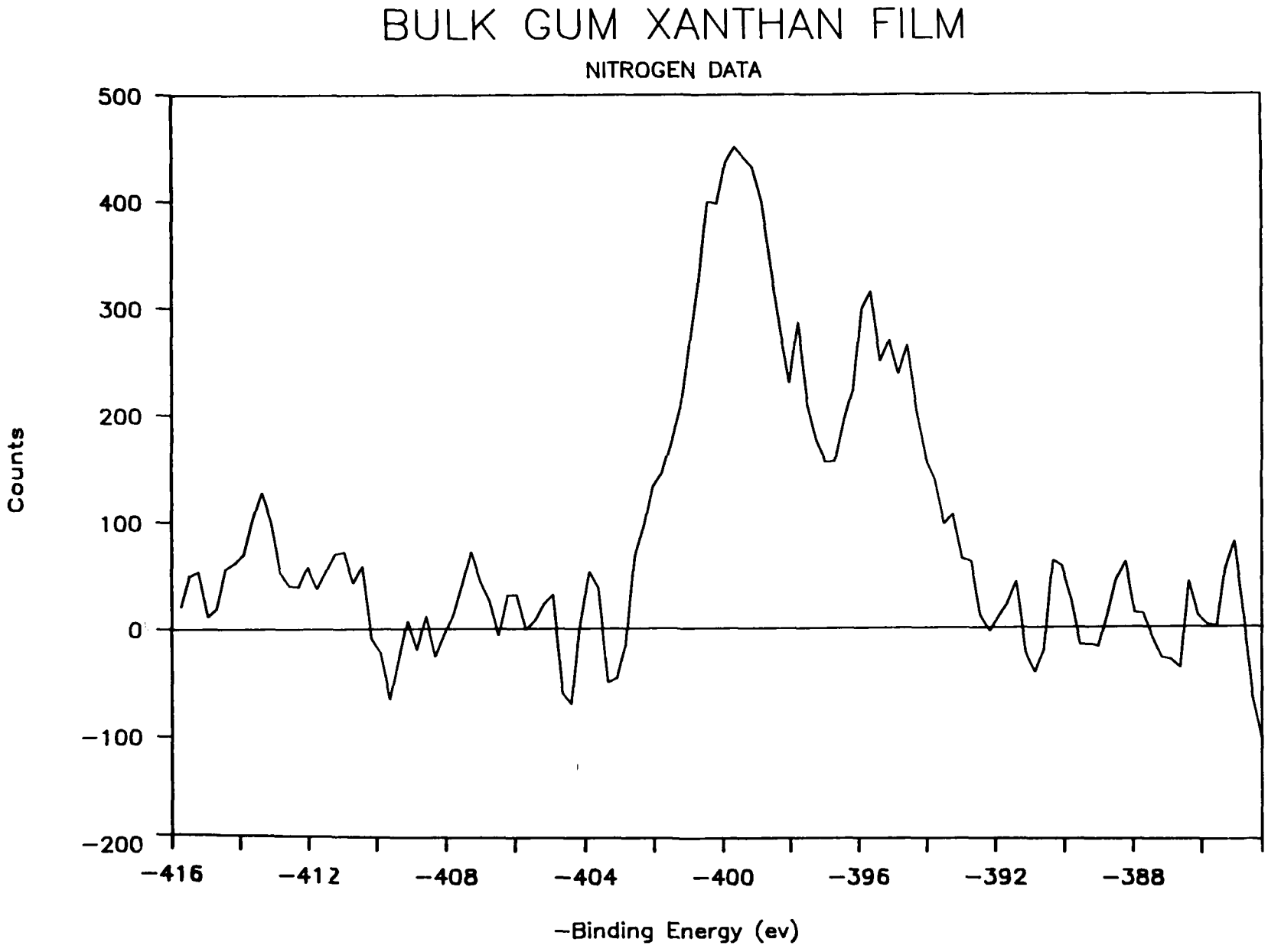


Fig. 9. ESCA Nitrogen Signal of Gum Xanthan

in the signal can be clearly seen. The major component is at 399 ev, similar to the protein signal, while the minor component (ratio 1/1.3) is at 395.5. The minor component appears similar to a much smaller fraction of a minor component in the nitrogen signal of the protein, which can be visualised as a small shoulder near the baseline in Fig. 5. The major component of the gum-x nitrogen signal may reflect a small fraction of peptide material in the exudate. The other component may reflect a fraction of other nitrogen-containing material, such as N-acetylated saccharides in the carbohydrate chains, because it is more than can be accounted for by the major protein-like signal. There is no significant gum sulfur signal.

d. Humic Extract. Humic substances are complex products which form when compoments of biological organisms are released into the environment. The release may occur because the organisms secrete material during their normal life cycle, or because they decompose and release their constituents on degeneration and death. In either case, soluble material, (such as the protein, carbohydrate, small metabolites, and nucleic acid components), and the lipid components which can be solubilised when they complex with soluble organics, react in the environment. They are processed by microorganisms and by non-biological reactions whose details are still obscure [7]. These processes result in an aqueous form of humus in aquatic environments, and a terrestrial form on land. In coastal regions soil runoff carries large quantities of terrestrial humic substances into estuarine waters. The humic substances are not easily metabolized directly by most organisms in natural waters and therefore have long lifetimes in the aquatic environment [8]. Although not very nutritive, they are surface-active [9], and therefore the degree to which they adsorb to immersed surfaces in competition with other adsorbates is important in the succession of events on the surfaces of immersed materials. The sample used in this work was a soil extract prepared commercially, and re-

extracted in our laboratory with ASTM artificial sea water which had been diluted to 12 parts per thousand salinity.

Fig. 10. shows the carbon signal of the humic extract sample. This signal is similar to the protein signal in two respects. First, the binding energy of the major component is 284 ev. Secondly, the minor component (1/10) has a higher binding energy than the major component, at 288-289 ev.

Fig. 11. shows the oxygen signal of humic extract. As is true for the protein, carbohydrate, and exudate samples, there is a high binding energy major component and a low energy minor (ratio 1/2.6) component. The major component is at 532 ev, similar to the carbohydrate samples, rather than to the protein sample at 530.5 ev. The minor components in all these cases have similar binding energy, at 527.5 ev.

Fig. 12. shows the nitrogen signal of humic extract. This signal is weaker than the gum xanthan nitrogen signal by a factor of 2 (normalized with respect to the carbon signal), and so is more difficult to quantify. However, it is clear that the signals are qualitatively similar, in that the signal also has two main components at similar binding energies. Therefore, a similar interpretation may be suggested.

Fig. 13. shows the sulfur signal of humic extract. The signal is at 169 ev, which is quite high. Such signals are characteristic of sulfur bound to electronegative atoms, such as oxygen. Therefore, this signal may indicate binding of bay water sulfate ions to the humic extract. There is no significant sulfur signal similar to the protein -SH or -SS-. Because the humic material is the result of many complex transformations of protein, carbohydrate, and other biogenic components, detailed analysis might be expected to show that the structure and signals of humic substancees vary, reflecting the conditions of their formation and aging.

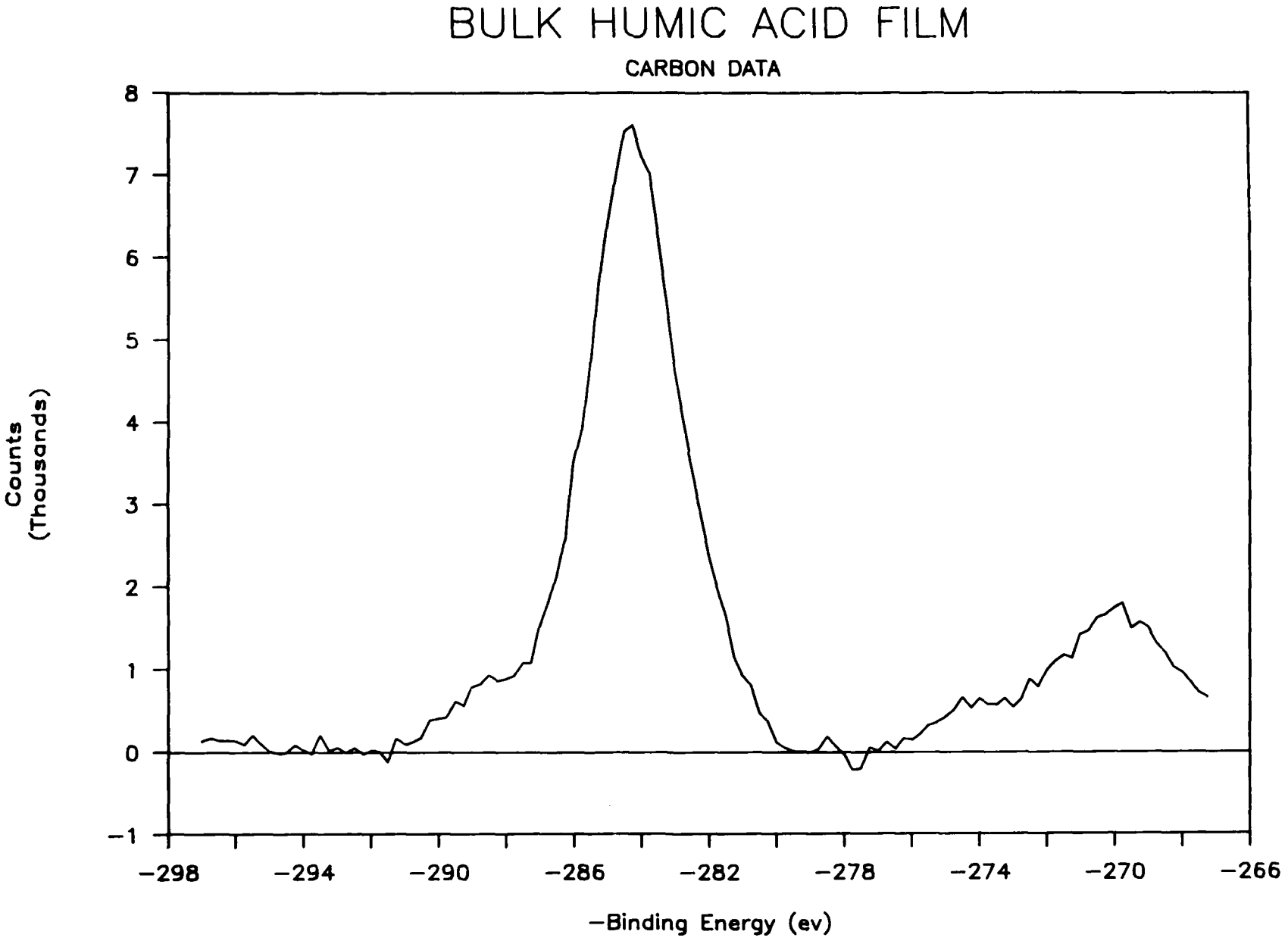


Fig. 10. ESCA Carbon Signal of Humic Extract

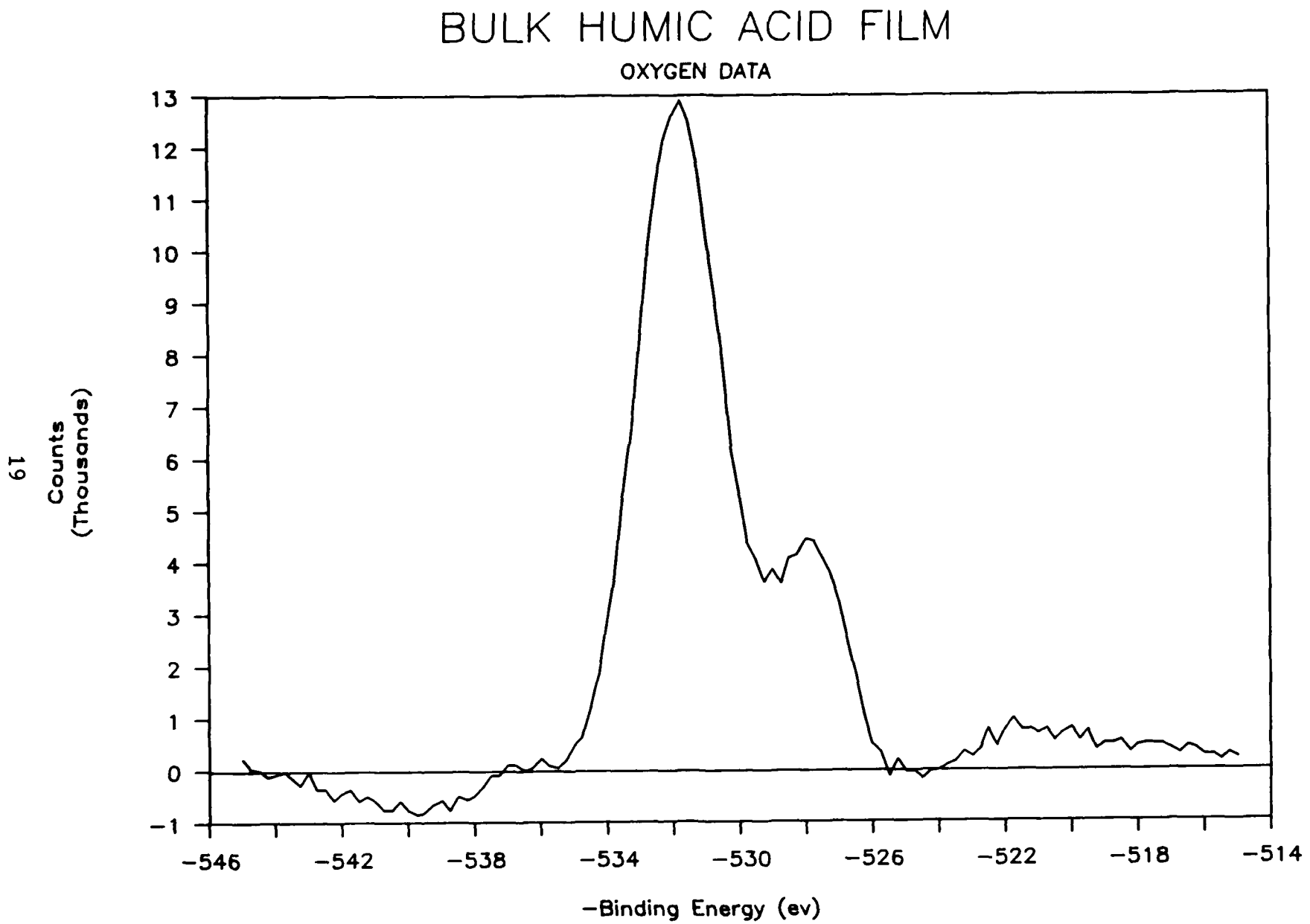


Fig. 11. ESCA Oxygen Signal of Humic Extract

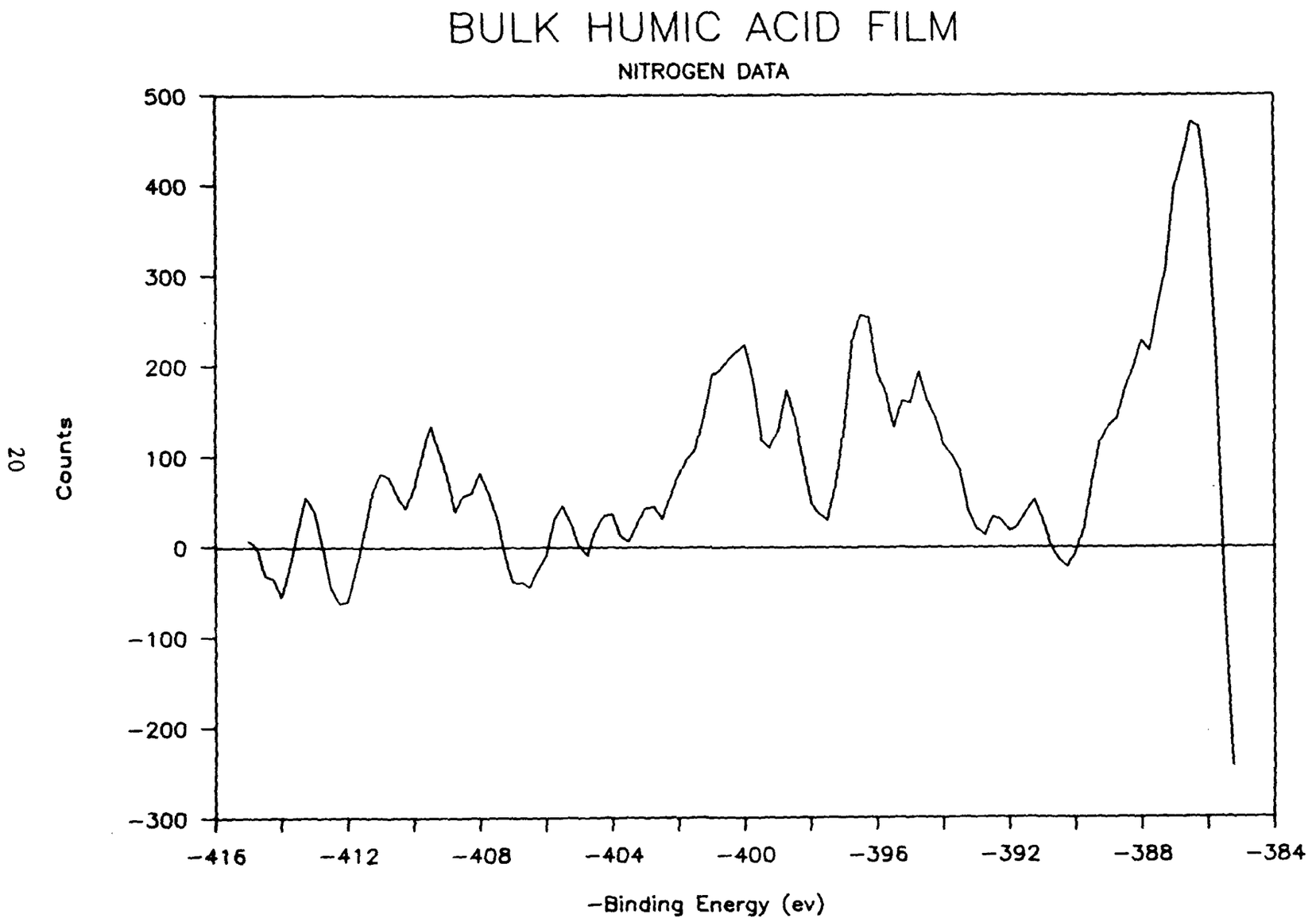


Fig. 12. ESCA Nitrogen Signal of Hunic Extract

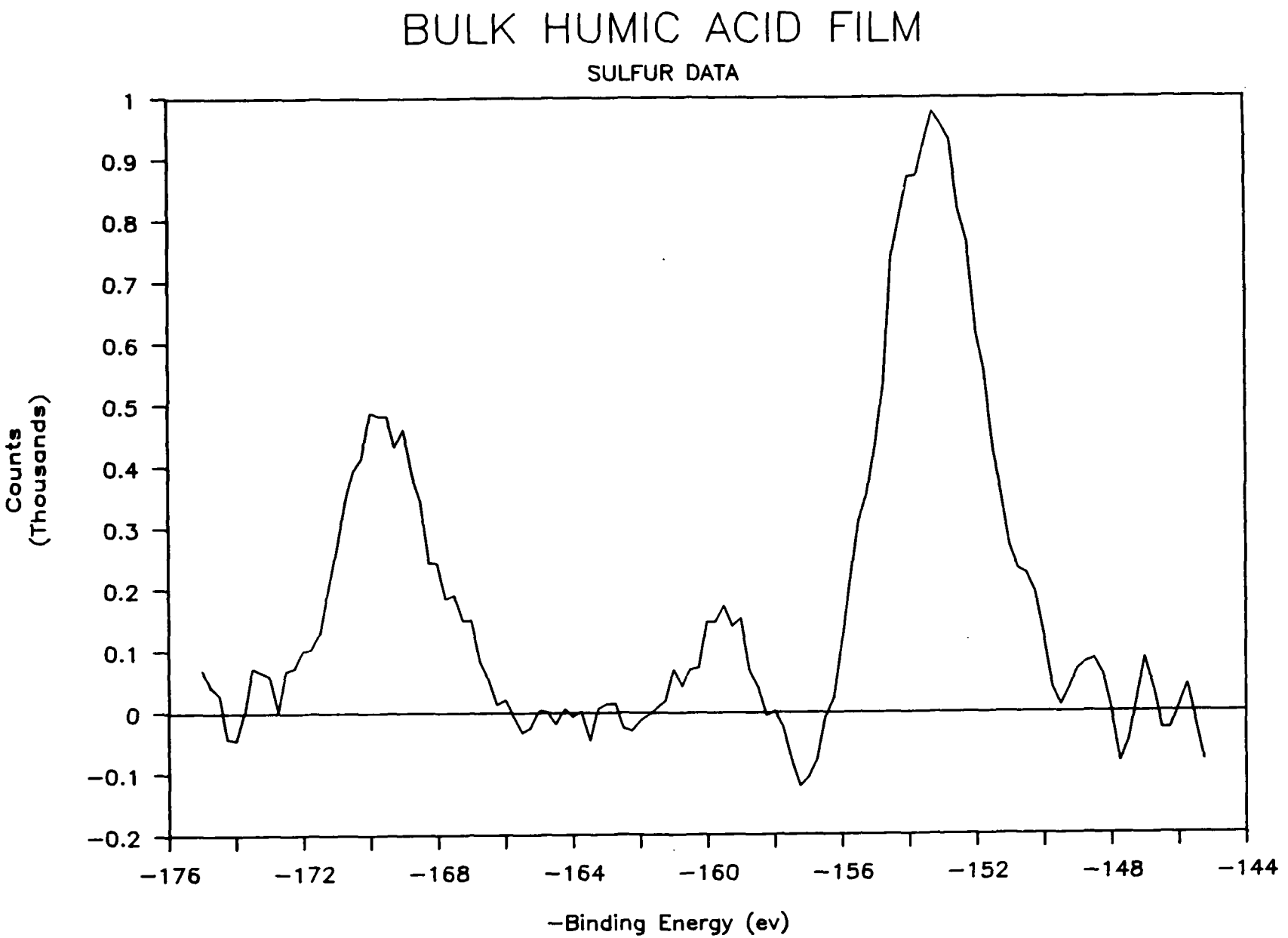


Fig. 13. ESCA Sulfur Signal of Humic Extract

EXPOSED MATERIALS:

a. Cupronickel Alloy (90/10); March. The adsorbed films formed during exposures in early spring did not show significant quantities of nitrogen or sulfur, whether exposed under freely corroding or cathodically protective potentials.

Figs. 14 and 16 show the carbon signals. The positions of the carbon signal maxima, at 284.5 ev, and the presence of a minor component at higher binding energy, are similar to the signals obtained from protein and humic acid rather than carbohydrate.

As shown in Figs. 15 and 17, the oxygen signal for the freely corroding case is significantly different than for the cathodically protected case. The freely corroding sample signal shows a pronounced minor component at lower binding energy, similar to the humic acid signal. On the other hand, the cathodically protected sample signal is much more symmetrical, showing a single component whose binding energy (531 ev) is similar to the major component of the freely corroding sample. This binding energy is similar to that of the major component of the humic extract.

b. Cupronickel Alloy (90/10); May. Figs. 18 and 19 show the carbon signals, which have maxima at positions similar to the March samples, and the cathodically protected sample has a similar high binding energy component. This minor component is less noticeable in the film from the freely corroding sample.

Figs. 20 and 21 show the oxygen signals. The cathodically protected sample signal is similar to the oxygen signal of protein, with components at 530 and 527.2 ev, and a similar ratio (2.6). The freely corroded sample signal shows a more prominent minor component, but this results from a greater separation of the components: the major component is at 531.5 ev, and the minor component

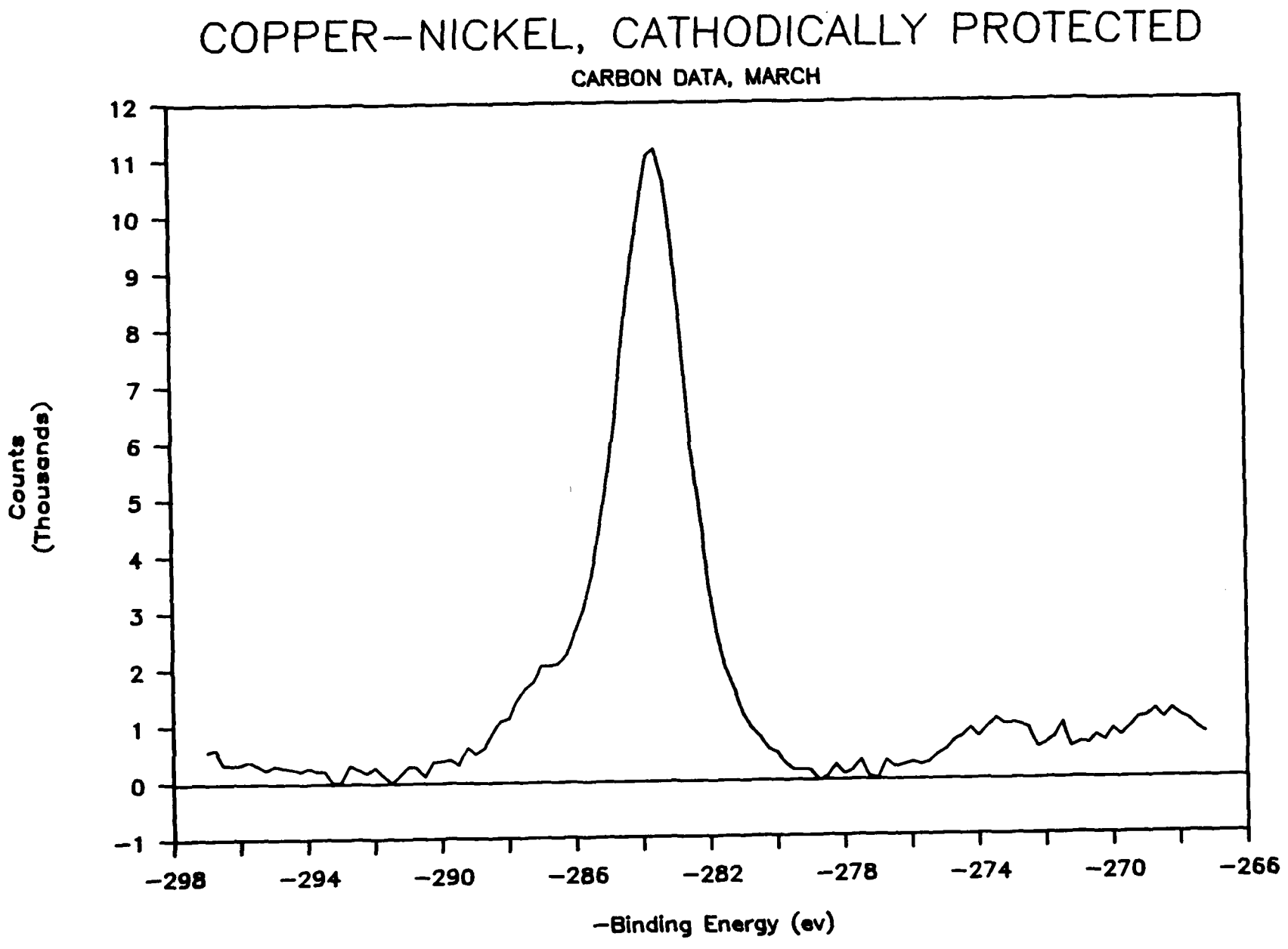


Fig. 14. ESCA Carbon Signal of Exposed Copper Nickel Sample, Cathodically Protected (March)

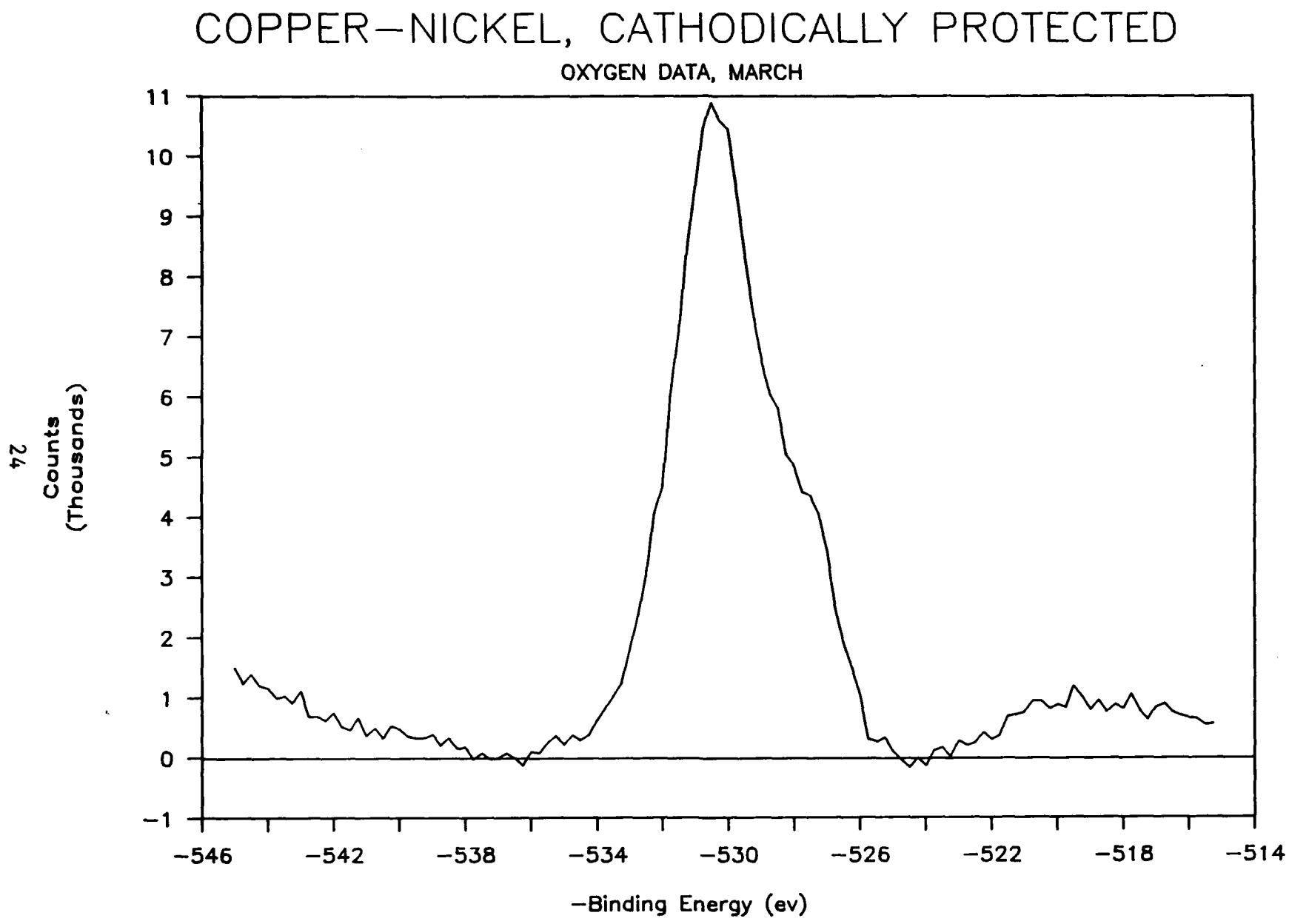


Fig. 15. ESCA Oxygen Signal of Exposed Copper Nickel Sample, Cathodically Protected (March)

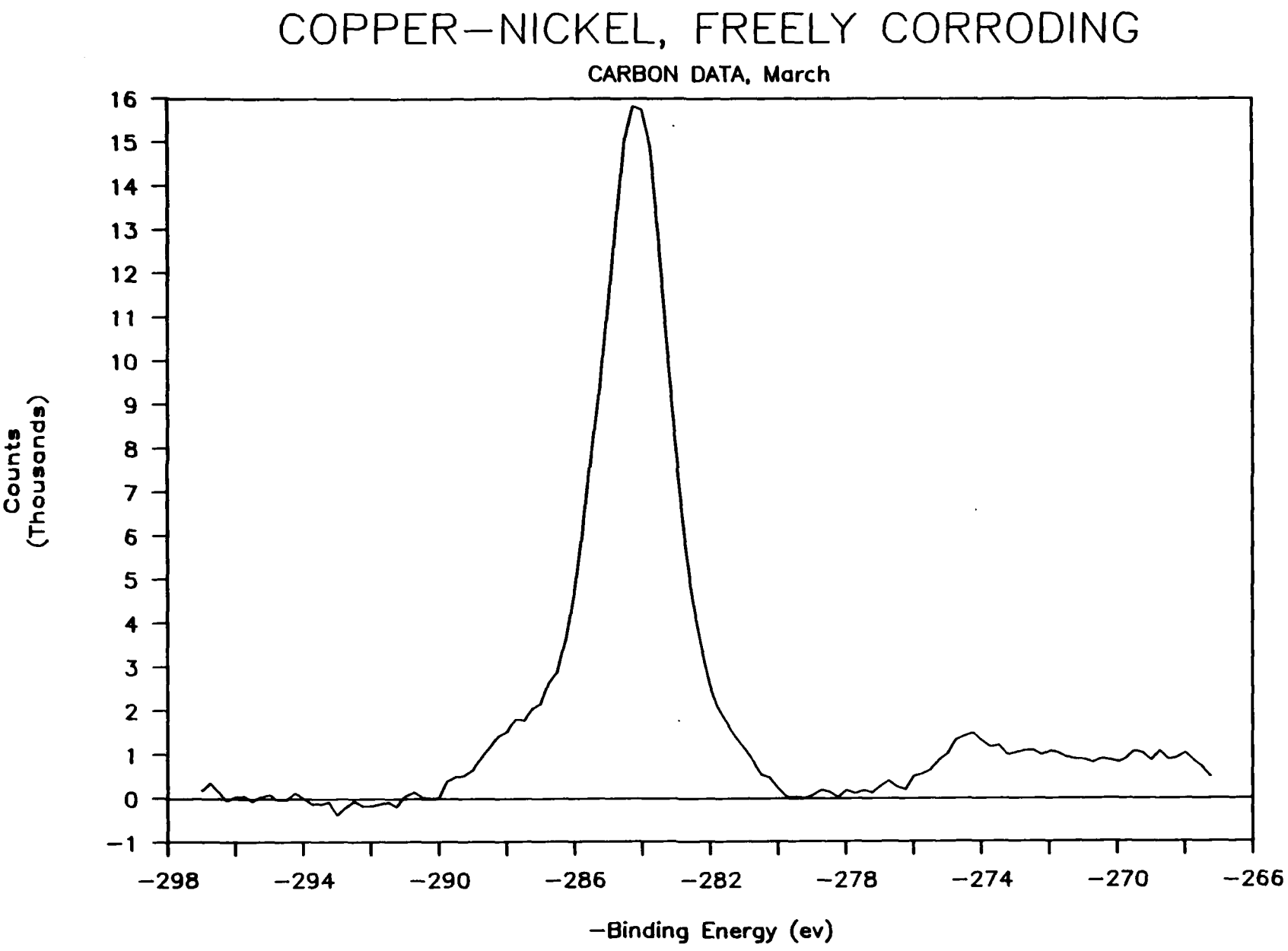


Fig. 16. ESCA Carbon Signal of Exposed Copper Nickel Sample, Freely Corroding (March)

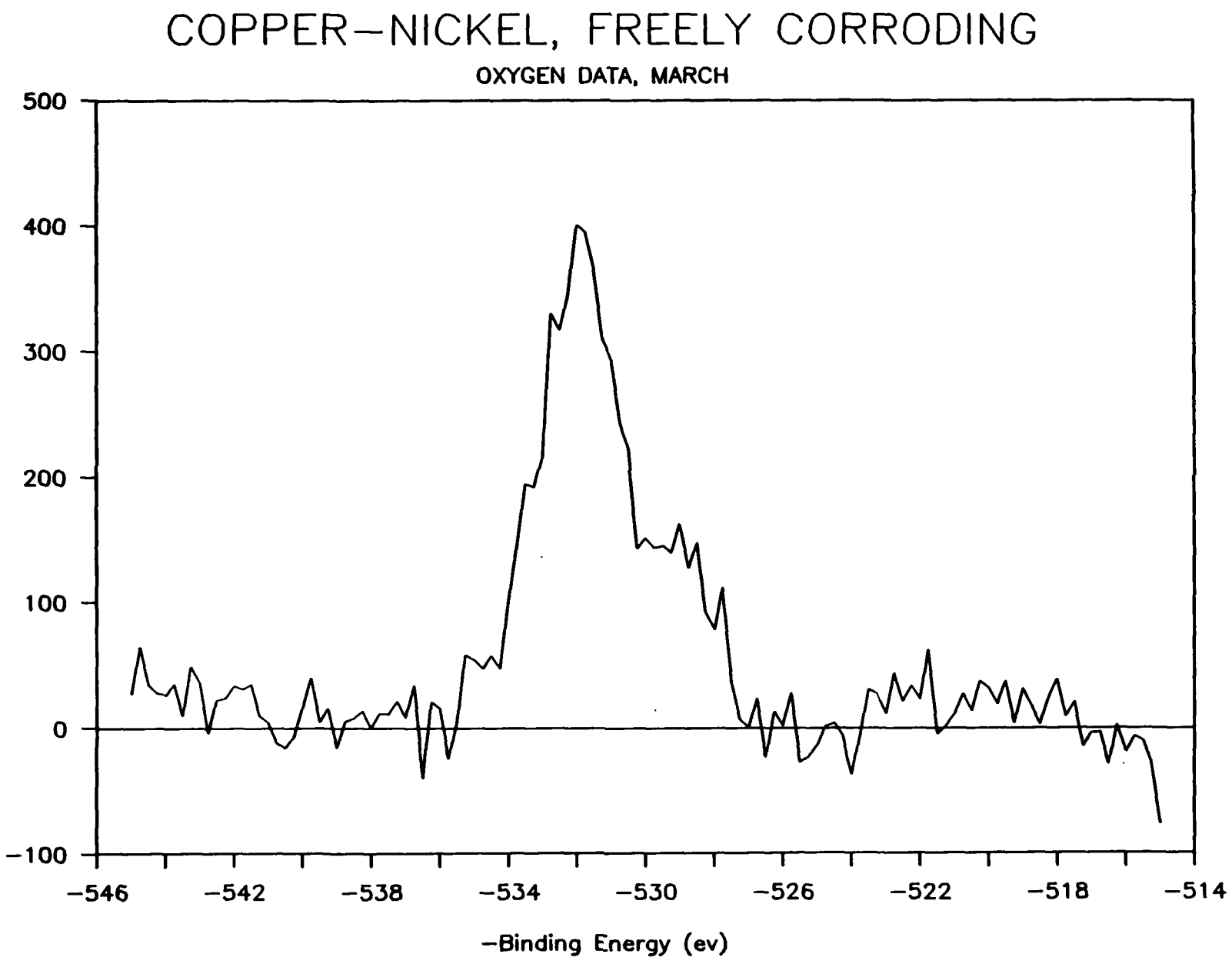


Fig. 17. ESCA Oxygen Signal of Exposed Copper Nickel Sample, Freely Corroding (March)

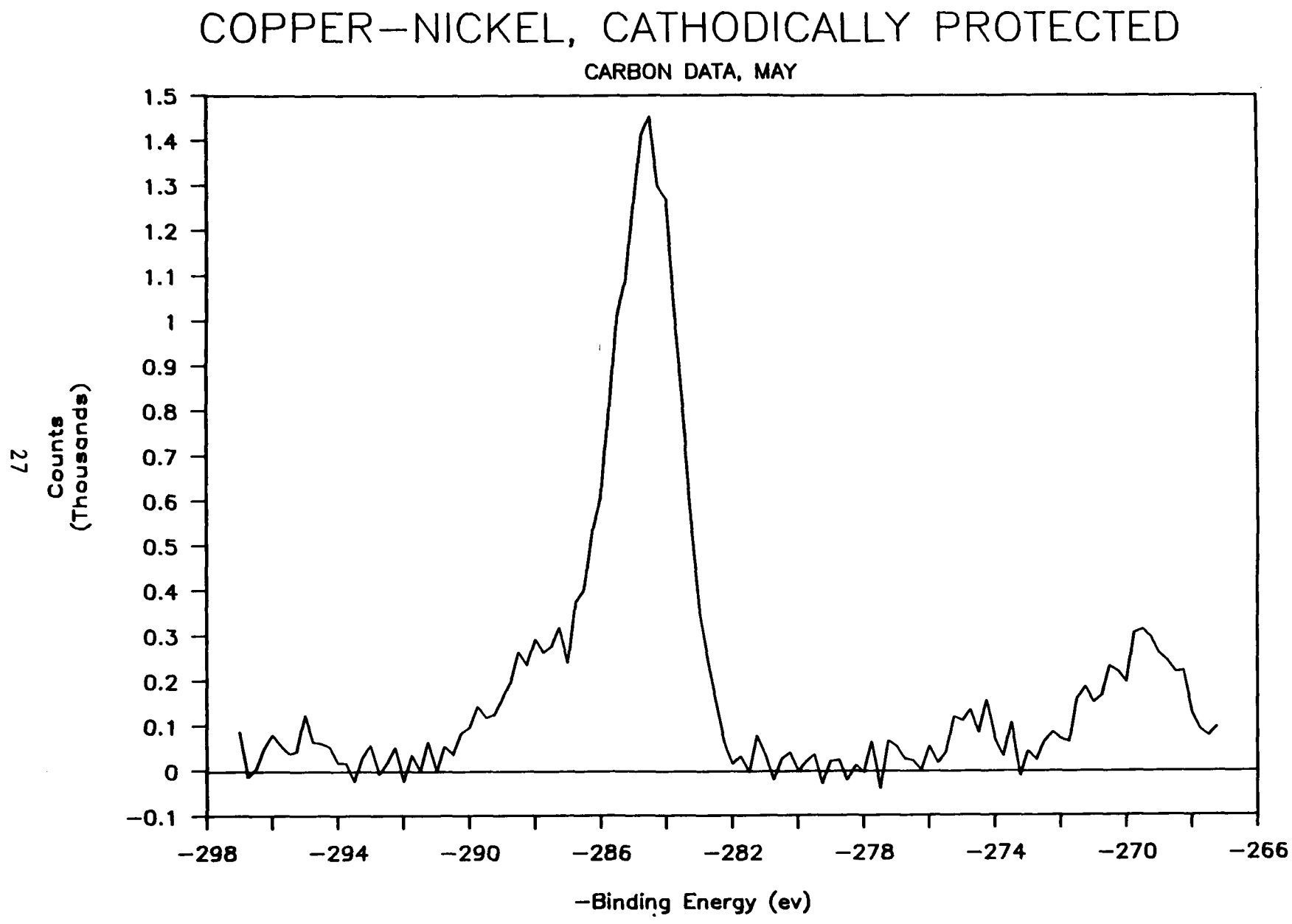


Fig. 18. ESCA Carbon Signal of Exposed Copper Nickel Sample, Cathodically Protected (May)

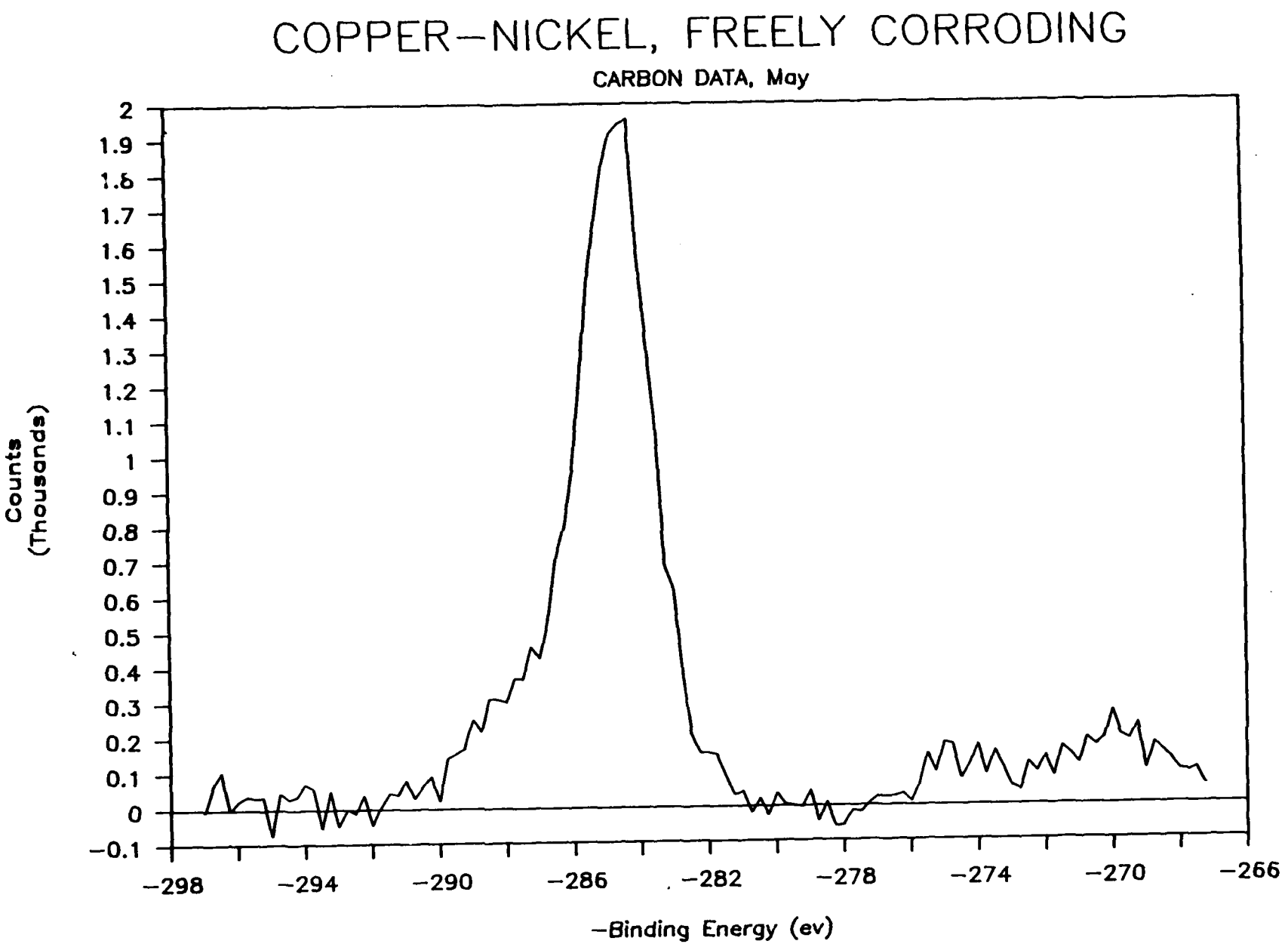


Fig. 19. ESCA Carbon Signal of Exposed Copper Nickel Sample, Freely Corroding (May)

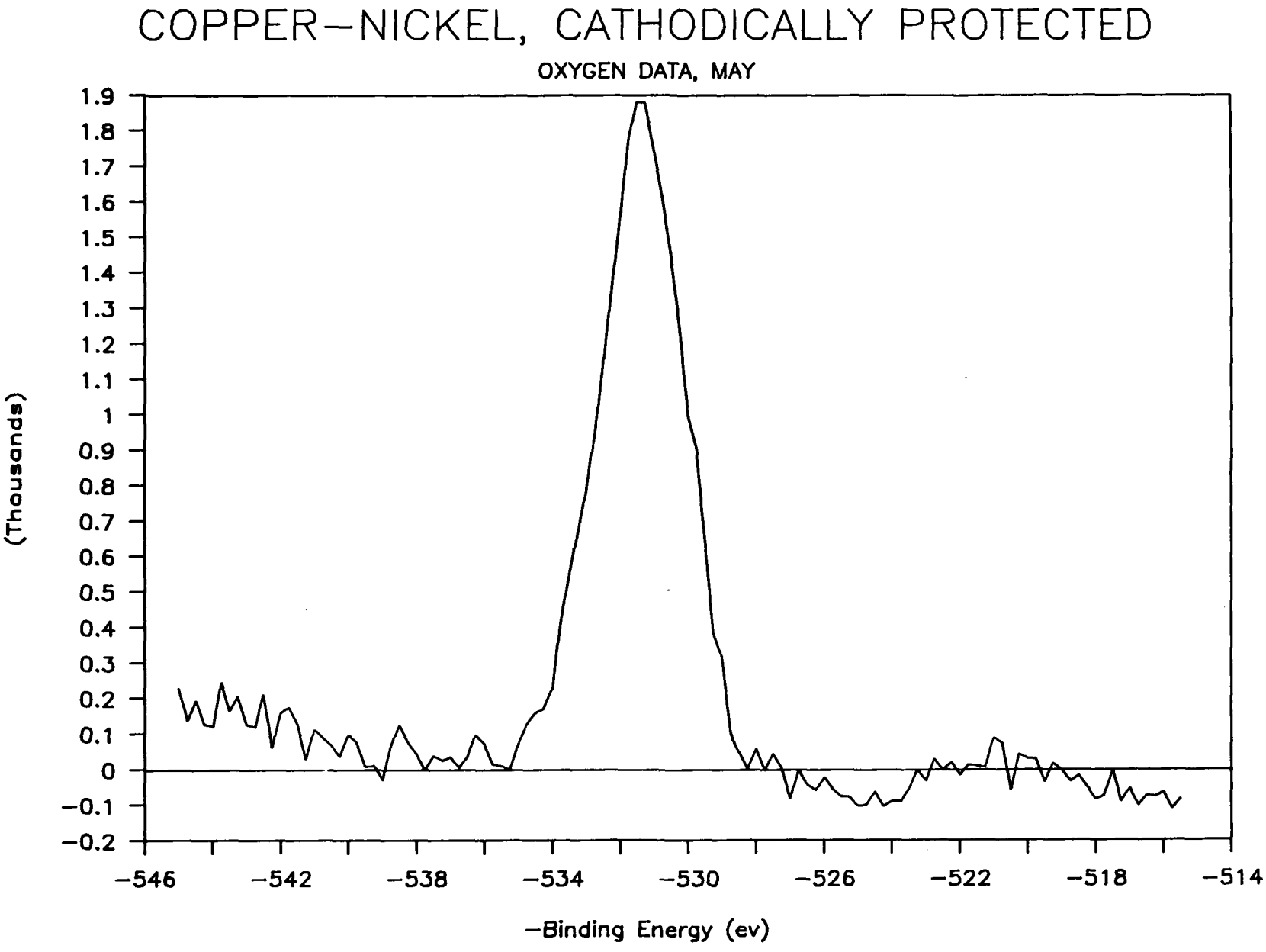


Fig. 20. ESCA Oxygen Signal of Exposed Copper Nickel Sample, Cathodically Protected (May)

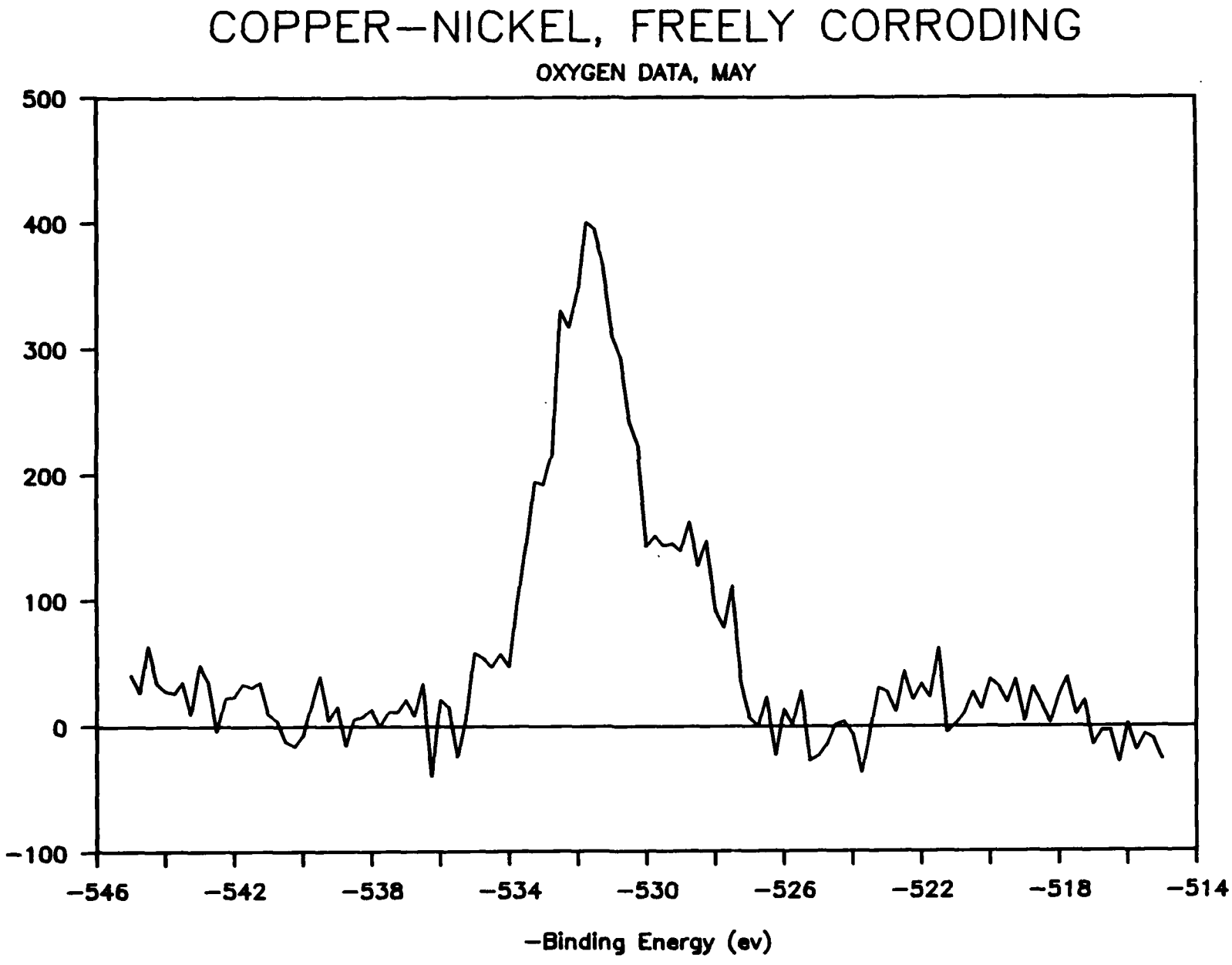


Fig. 21. ESCA Oxygen Signal of Exposed Copper Nickel Sample, Freely Corroding (May)

(ratio 1/2.6) is at 527.4. This is similar to the humic extract signal.

Figs. 22 and 23 show the nitrogen signals. The cathodically protected sample signal is a single major component, as was the protein signal. The freely corroding sample signal, however, indicates two well separated components similar to the humic extract and exudate signals.

Figs. 24 and 25 show the sulfur signals. Both the cathodically protected and freely corroding samples yielded significant sulfur signals. The cathodically protected sample signal is a narrower distribution, and is at 161 ev. This binding energy and width are consistent with metal sulfide signals [2], and it is therefore suggested that sulfides are present and are the predominant species of sulfur in this case. The freely corroding sample signal showed a broad distribution of binding energies similar to the protein signal of Fig. 6. However, the distribution is about 2 ev lower in binding energy than the protein, and the major component does not coincide with the expected value for disulfide groups. It is shifted towards the values at lower binding energy characteristic of metal sulfides, although the distribution is sufficiently broad that a variety of species and environments of the sulfur atoms can be consistent with it.

c. PVC [Poly(vinyl chloride)]; May. This polymer is a commonly used material in marine environments, for piping as well as for structural members. The material before exposure shows both carbon and oxygen signals: no nitrogen or sulfur signals are evident either before or after exposure.

Fig. 26. shows the carbon signals for PVC. The signal is a single peak at 284 ev for the clean sample, and moves to 285 ev after exposure.

Fig. 27. shows the oxygen signals for PVC. The signals are doublets: at 529 and 532 ev for both the clean sample and after exposure. The ratio of carbon to oxygen signal area is 0.5 before and 0.6 $\pm$ after exposure, and the

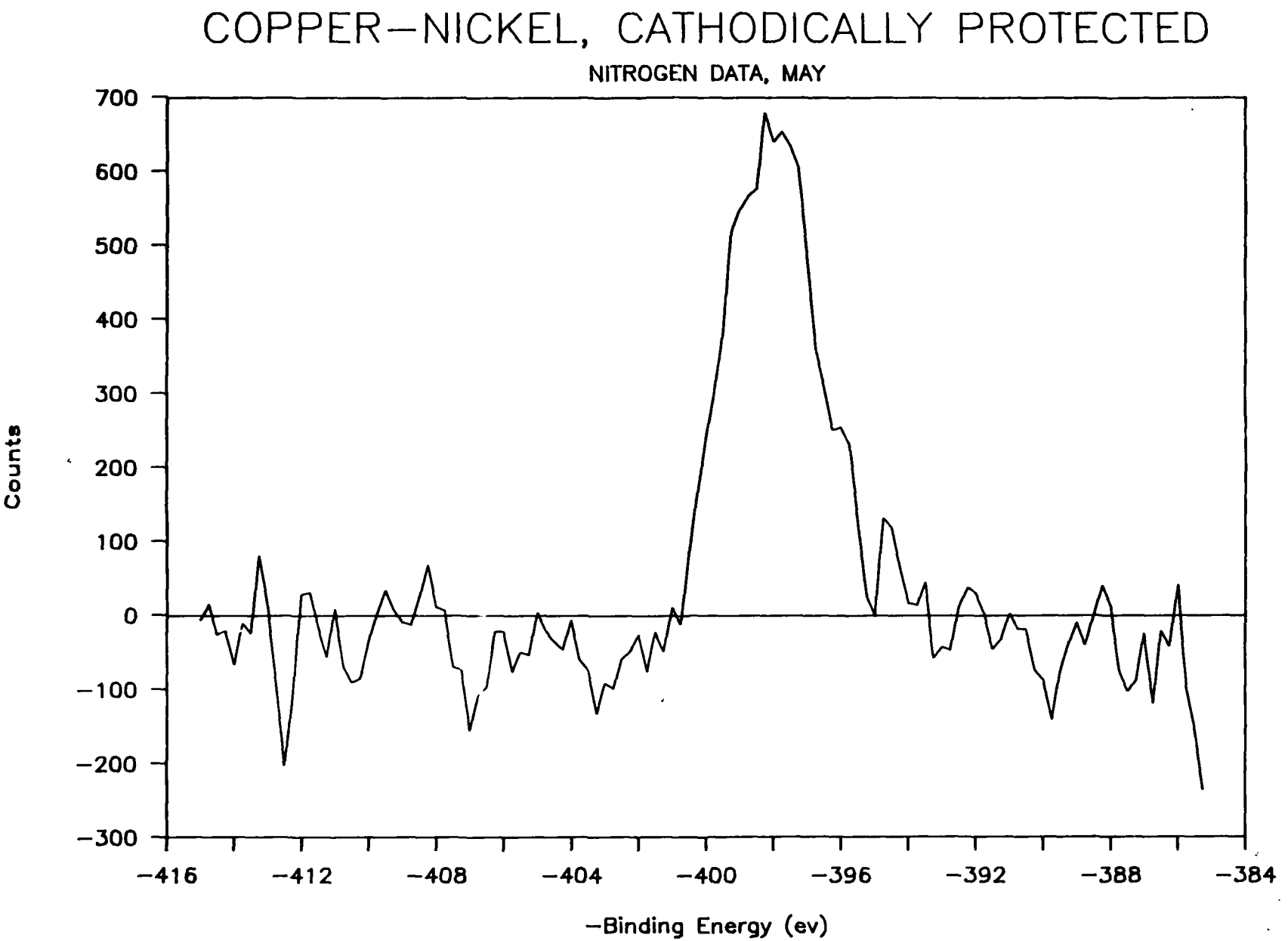


Fig. 22. ESCA Nitrogen Signal of Exposed Copper Nickel Sample, Cathodically Protected (May)

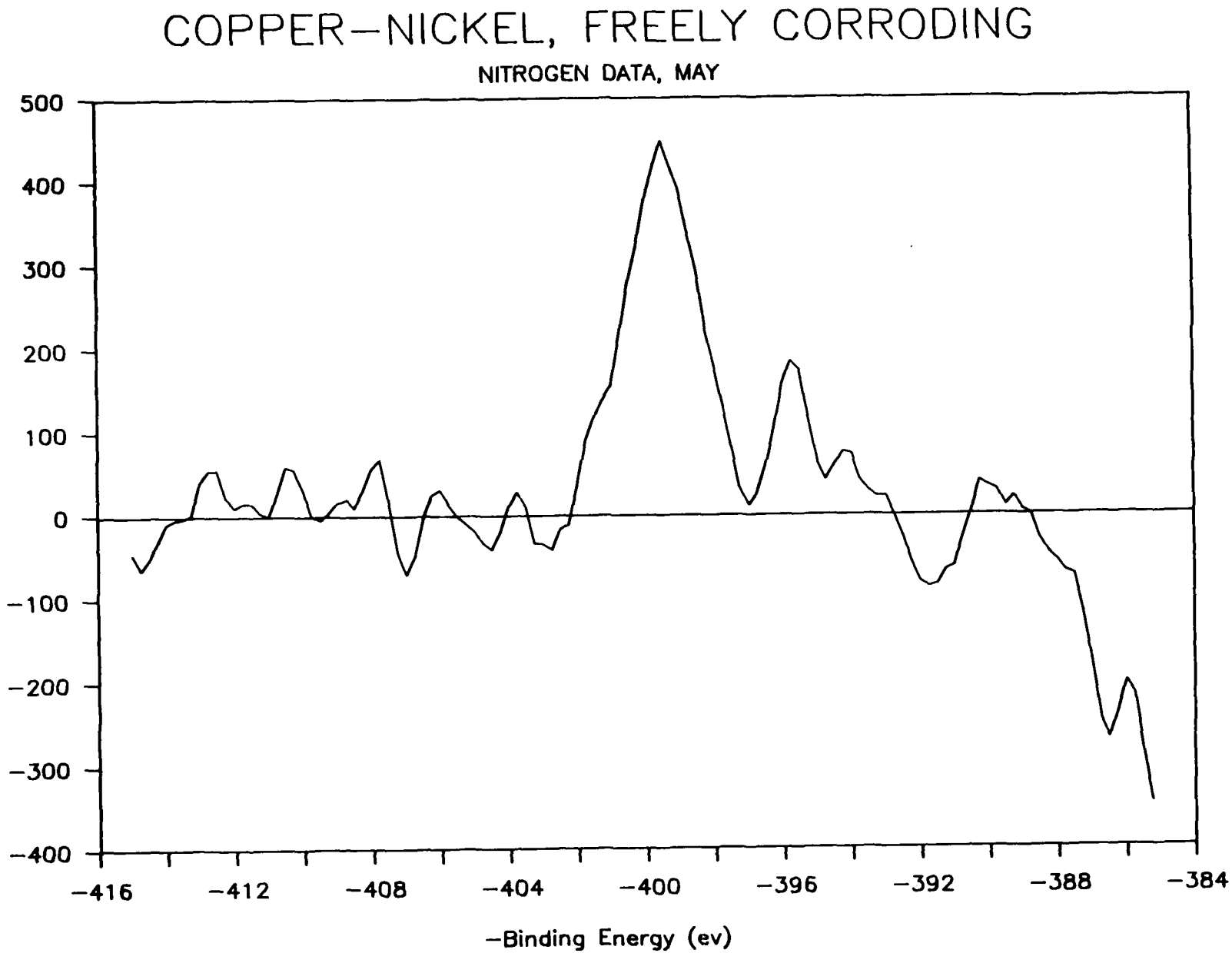


Fig. 23. ESCA Nitrogen Signal of Exposed Copper Nickel Sample, Freely Corroding (May)

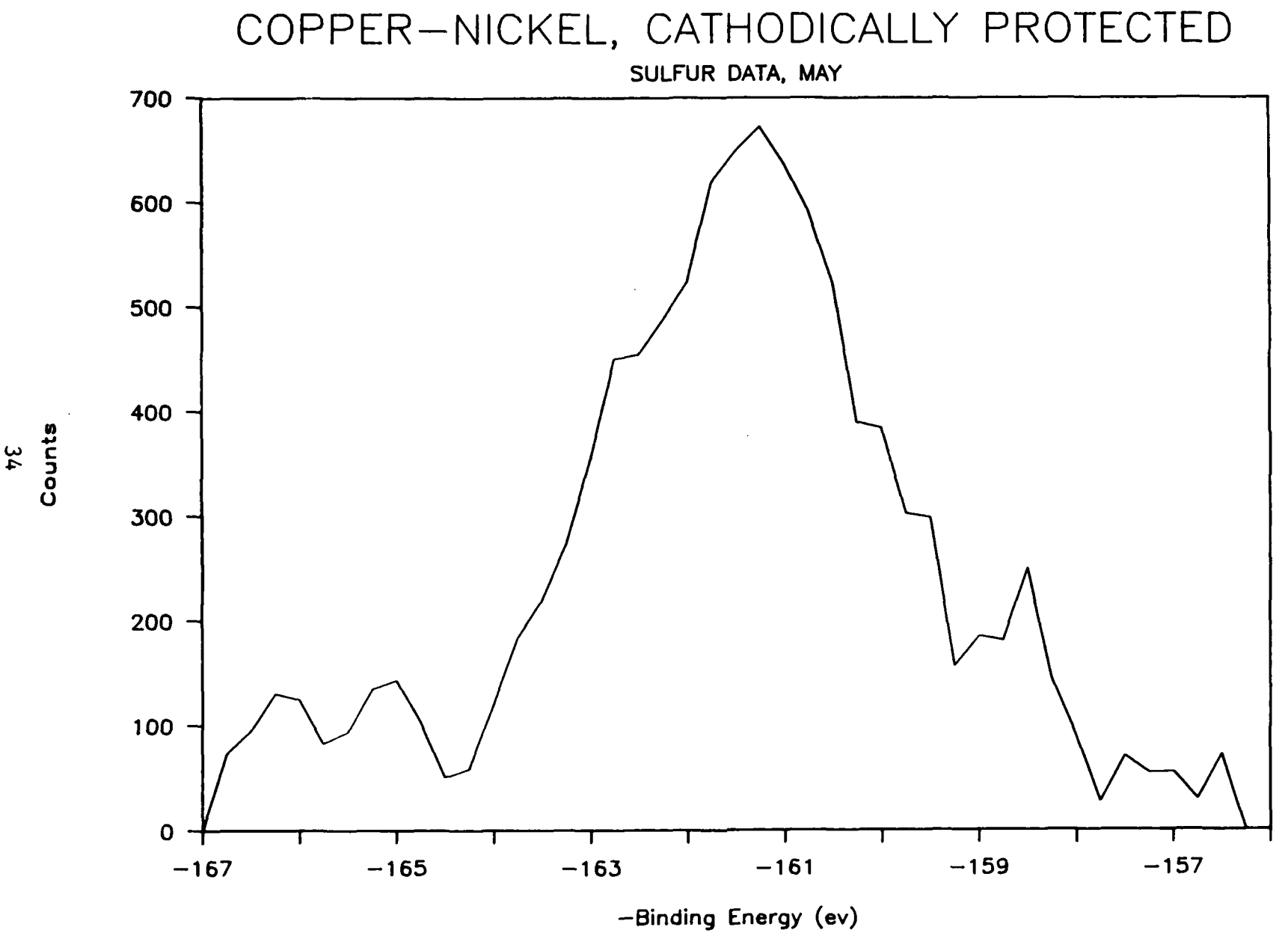


Fig. 24. ESCA Sulfur Signal of Exposed Copper Nickel Sample, Cathodically Protected (May)

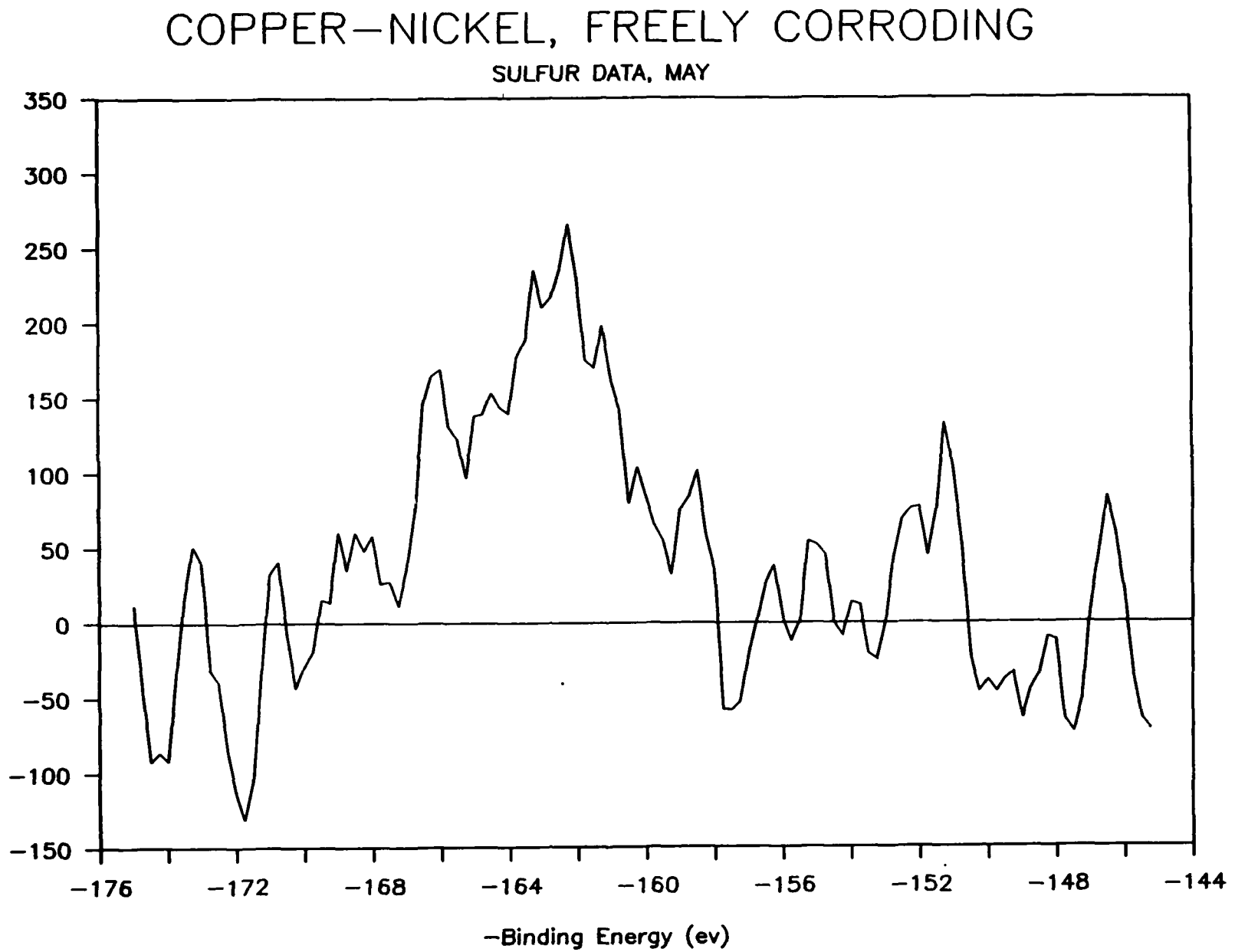


Fig. 25. ESCA Sulfur Signal of Exposed Copper Nickel Sample, Freely Corroding (May)

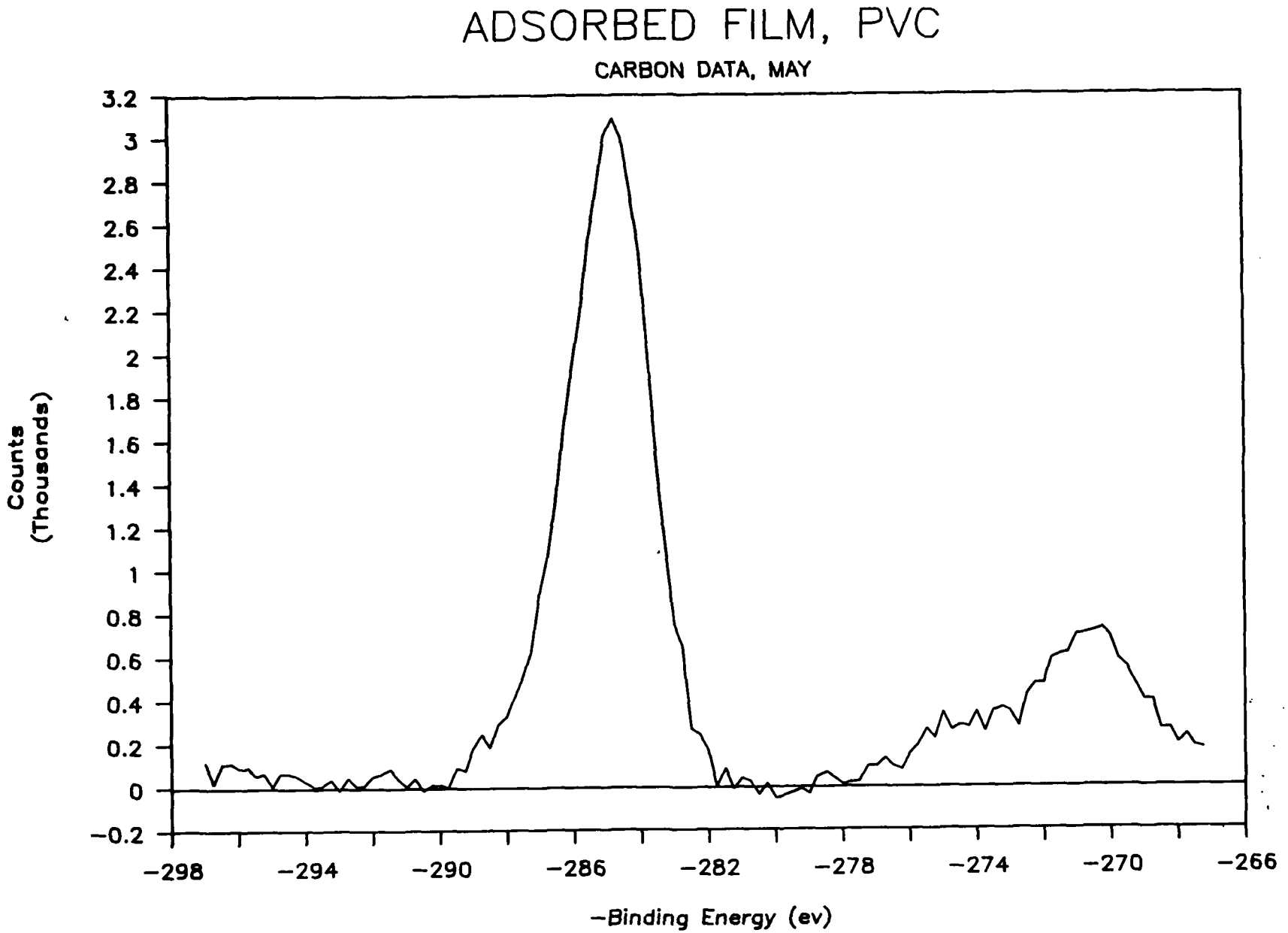


Fig. 26. ESCA Carbon Signal of Exposed PVC

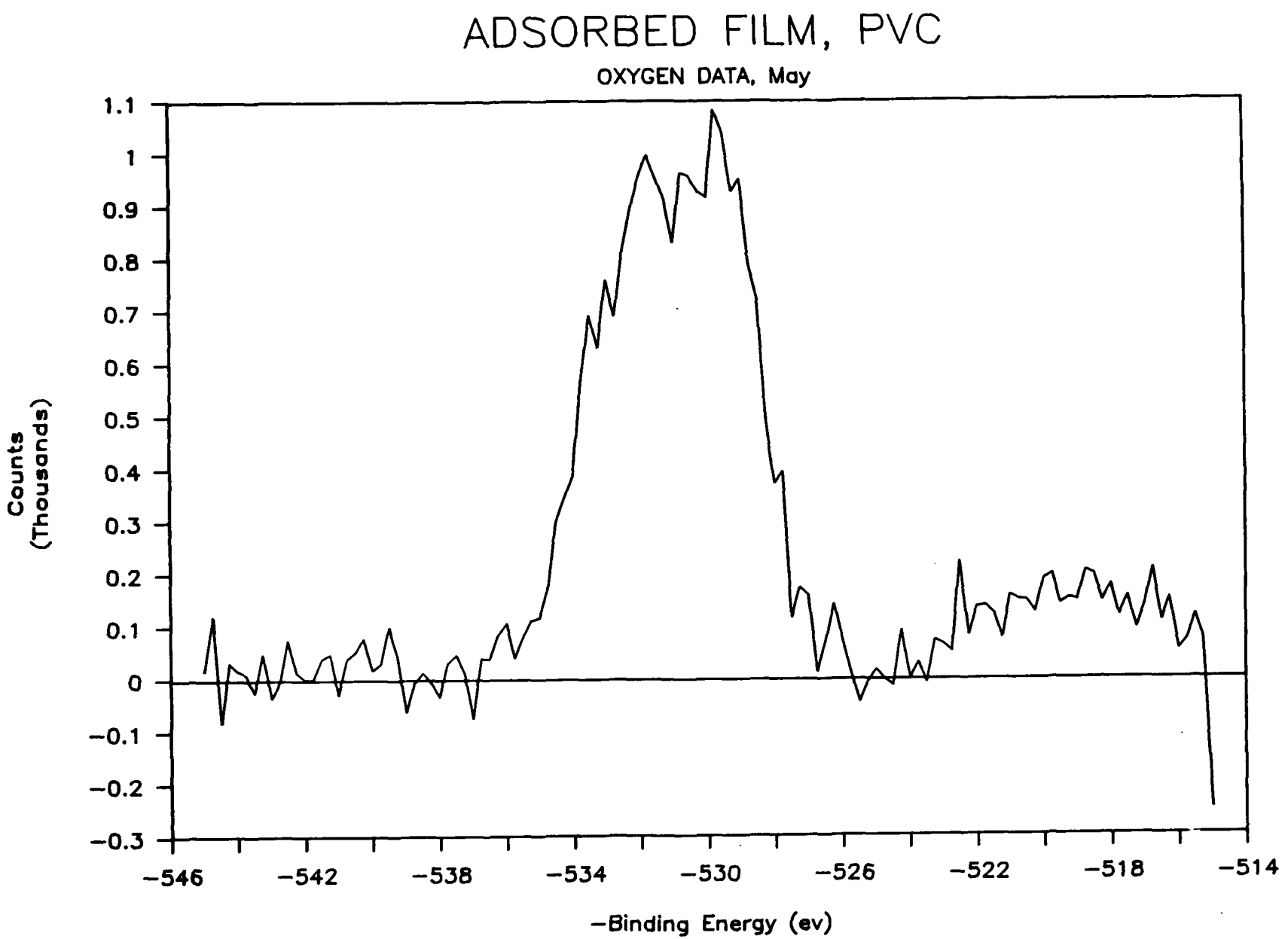


Fig. 27. ESCA Oxygen Signal of Exposed PVC

ratio of the areas of the 532 to the 529 ev peaks is 1.1 before as well as after exposure. There is, then, no unequivocal indication of a difference in surface chemistry or of a stable film on the PVC sample after exposure.

d. FEP [Poly(perfluoroethylene-propylene)]; May. This polymer, a member of the Teflon series, has very low surface free energy, and therefore has been of great interest both from the point of view of adhesion theory and as a practical non-stick material. The degree to which the surface of fluoropolymers sustains an adsorbed film is a significant parameter in any explanation of adhesion in natural waters.

Fig. 28. shows the carbon signals for FEP. The clean material shows two well-separated components: the major one at 284 and another at 290 ev, with area ratio 3. After exposure, the signals are at 285 and 292 ev, and the ratio is unity when peak width is accounted for.

Fig. 29. shows the oxygen signals for FEP. The signal given by the clean material is clearly skewed, and can be resolved to two signals: the major one at 528 and another at 531 ev, with area ratio 1.3. After exposure, the area ratio is 1.1. The oxygen/carbon signal area ratios are 0.61 before and 0.66 after exposure. Thus, a significant change has occurred in the FEP surface during exposure, especially noticeable via the carbon signal. This by itself, however, is not sufficient to allow further meaningful statements about the nature of the effect, especially in the absence of nitrogen or sulfur information or of other supplementary data.

The very distinctive carbon signal of FEP, which reflects the influence of the electronegative fluorine atoms upon the carbon binding energy, is a convenient indicator for the degree of coverage of the surface in comparison with the sampling depth of the ESCA method. The change in signals indicates a perceptible

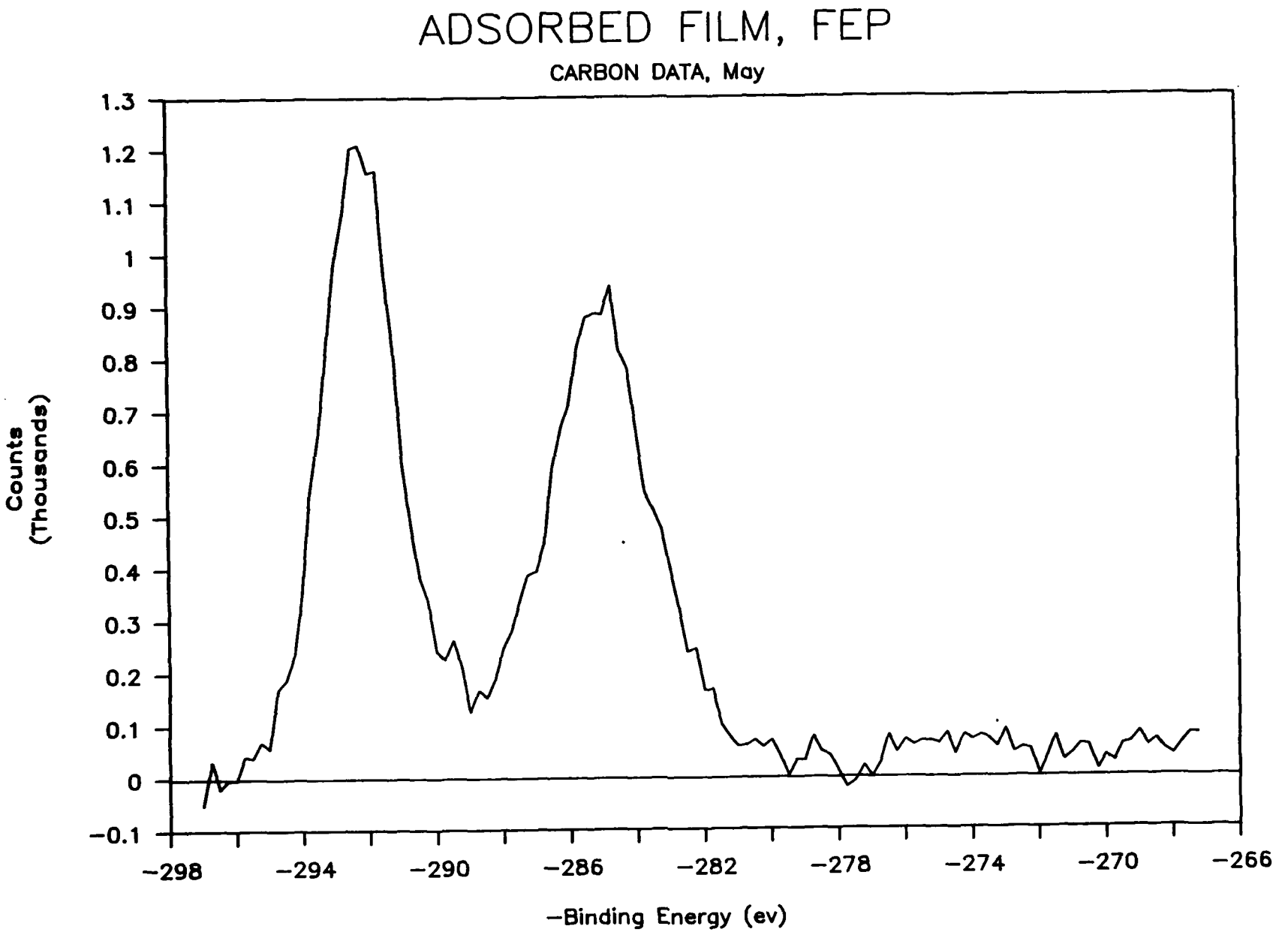


Fig. 28. ESCA Carbon Signal of Exposed FEP

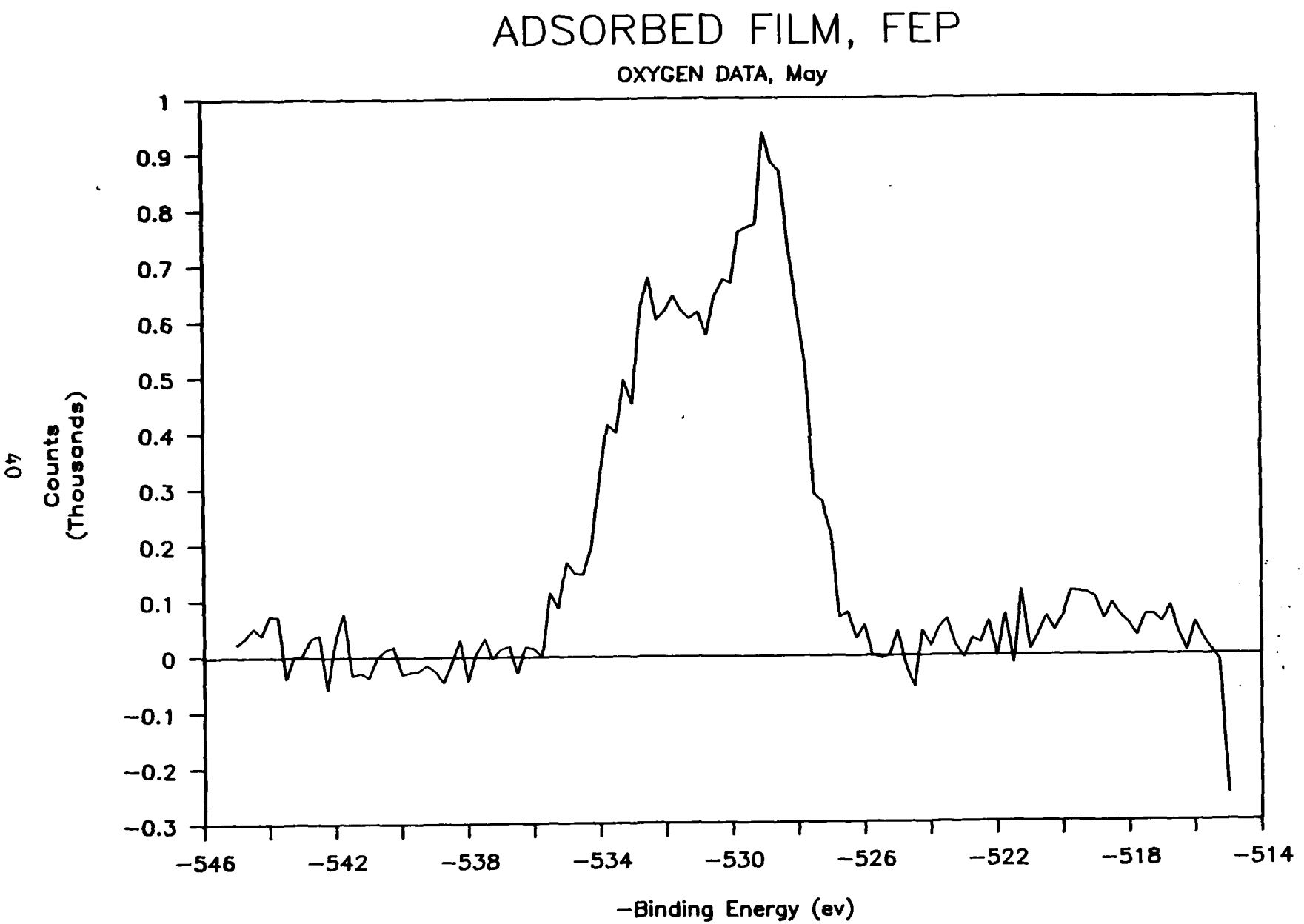


Fig. 29. ESCA Oxygen Signal of Exposed FEP

change in the surface, but the persistance of the 290 ev signal indicates the coverage is limited. The lack of nitrogen and sulfur signals at the same season as the second cupronickel exposure also emphasizes that the adsorption process quite different on the PVC and FEP than on the alloy.

Neither the FEP nor the PVC polymer shows the presence of oxygen in its nominal formula. It is clear, however, that a sizeable quantity of oxygen is present in their surface regions. This oxygen is not loosely bound, because the ESCA experiment is conducted in vacuum, so that loosely bound material would be lost in the pump-down of the experimental chamber. A similar observation was made by Schrader and Cardamone using TFE [poly (tetrafluoroethylene)], another form of Teflon, in earlier work associated with this project [1]. These observations clearly demonstrate that surfaces of exposed polymers react in some way with oxygen. The resulting oxygenated surface properties are involved in the subsequent processes, rather than the surface properties which are expected on the basis of the bulk chemical composition. It is conceivable that the length of time of atmospheric exposure as well as the conditions of exposure will effect the surface of the polymer in a manner not closely correlated with measurements of bulk properties.

Table 1. shows the atomic ratios derived by integrating the areas under the high-resolution signals for the known compounds and the films adsorbed on the alloy. Using these data, the atomic composition of the adsorbed films can be characterized in terms of their similarity to the known substances.

The films resulting from the March exposures can be seen to contain very little nitrogen or sulfur in comparison with the strength of the carbon signal. This is similar to the ratios characteristic of the humic extract and carbohydrate. The cathodically protected sample's oxygen signal was similar to that of a

carbohydrate, although shifted to higher binding energy, perhaps as a result of copper interaction. The freely corroding sample's oxygen signal, in contrast, was similar to that of the humic extract.

The films resulting from the May exposure were dramatically different. These films had prominent nitrogen and sulfur signals, of the magnitude of

Table 1. Atomic signal ratios for organic films

| | Nitrogen/Carbon | Sulfur/Carbon |
|---|---|---|
| Standard Materials: | | |
| Carbohydrate | 0.03 | 0.005 |
| Humic Extract | 0.03 | 0.005 |
| Protein | 0.4 | 0.03 |
| Cupro-Nickel ( May ) | | |
| Freely Corroding | 0.2 | 0.02 |
| Cathodically Protected | 0.3 | 0.05 |
| Cupro-Nickel ( March) | | |
| Freely Corroding | 0.05 | 0.005 |
| Cathodically Protected | 0.05 | 0.005 |

proteins. Their carbon signals were similar to protein or humic extracts, and, as in the case of the March samples, the oxygen signals were different in the two electrochemical situations. The cathodically protected sample signal showed a single component at the position of the major protein peak, while the freely corroding sample signal was similar to that of humic extract. The nitrogen signals were protein-like in the cathodically protected case, but more like the gum exudate or humic in the freely corroding case. The sulfur signals are also of great interest. The freely corroding sample showed a signal

which superficially seems similar to a protein sample, but the position of the signal is shifted towards lower binding energy. The central part of the signal is more towards the region where sulfides, rather than sulfhydryls or disulfides are expected. The cathodically protected sample signal is quite distinctive; it is what is expected for sulfide in both shape and binding energy.

These observations show that the surface modifications are sensitive to the electrochemical situation, and also to the water biochemistry. It is not surprising that the highly bioactive summer estuary will be rich in organic matter, and that it will be in a state closer to that of the original biological material, as reflected by its nitrogenous and more proteinaceous character, rather than the more humus-like, nitrogen and sulfur depleted material found after the winter. Therefore, phenomena such as complexation and solubilization by proteinaceous material and sulfide-induced attack on cupronickel should not be unexpected in this kind of environment. In addition, the more reducing cathodically protecting condition clearly results in a different film than the freely corroding case.

## CONCLUSIONS

1. The interaction of copper-nickel with dissolved matter in the local estuary yielded films which could be detected and characterized by ESCA.

2. The films on the copper-nickel alloy were of different nature when formed under different conditions.

3. The variables affecting the nature of the film included a) the biogeochemical state of the estuary, as determined by the season, and b) the electrochemical potential.

4. Immersion of a sample of the plastic poly [vinyl chloride] in May did

not result in perceptible adsorption.

5. Immersion of the plastic poly [fluoro-ethylene-propylene] in May resulted in a clear change of the carbon and oxygen ESCA signals, indicating significant adsorption. The lack of significant nitrogen and sulfur signals indicated a different adsorbed film than was present on cupronickel exposed at the same time.

6. The sulfur signals indicated a role of sulfide in the films adsorbed on copper-nickel in May.

7. There are indications of protein-like components of some of the films. This refines the definition of the cupro-organic complex found on immersed copper-containing alloys in previous work [1].

8. Both sulfides and protein-related components in natural saline waters have been implicated in accelerated corrosion of copper and its alloys. These findings indicate their detectability after short exposure, and show that their presence is related to the exposure conditions.

## RECOMMENDATIONS FOR FUTURE WORK

1. This evidence of film formation on immersed materials reveals some aspects of processes preceeding perceptible corrosion and fouling processes. Examination with complementary spectral techniques, such as reflection infra-red and fluorescence spectroscopy, will allow more definitive specification of these films.

2. Exposure of pre-filmed materials to corrosive and bioactive environments will determine the extent to which the films influence colonization and corrosion. It is possible that inhibition of these deleterious processes will be accomplished through proper surface treatment.

3. Electrochemical investigation of film formation on copper-containing alloys will be important in developing methods for inhibiting their corrosion in bioactive environments.

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